

Composite boson many-body theory for Frenkel excitons

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We present a many-body theory for Frenkel excitons which takes into account their composite nature exactly. Our approach is based on four commutators similar to the ones we previously proposed for Wannier excitons. They allow us to calculate any physical quantity dealing with N excitons in terms of "Pauli scatterings" for carrier exchange in the absence of carrier interaction and "interaction scatterings" for carrier interaction in the absence of carrier exchange. We show that Frenkel excitons have a novel "transfer assisted exchange scattering", specific to these excitons. It comes from indirect Coulomb processes between localized atomic states. These indirect processes, commonly called "electron-hole exchange" in the case of Wannier excitons and most often neglected, are crucial for Frenkel excitons, as they are the only ones responsible for the excitation transfer. We also show that in spite of the fact that Frenkel excitons are made of electrons and holes on the same atomic site, so that we could naively see them as elementary particles, they definitely are composite objects, their composite nature appearing through various properties, not always easy to guess. The present many-body theory for Frenkel excitons is thus going to appear as highly valuable to securely tackle their many-body physics, as in the case of nonlinear optical effects in organic semiconductors.

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I. INTRODUCTION

Even if nature makes things somewhat more complex, we can roughly say that there are essentially two types of excitons: Wannier excitons [1] and Frenkel excitons [2].

(i) Wannier excitons are found in conventional (inorganic) semiconductors. They are constructed on valence and conduction extended states. Their Bohr radius, controlled by Coulomb interaction between electrons and holes, screened by the semiconductor dielectric constant, is as large as a few tens of interatomic distances. This makes their binding energy rather small.

(ii) Frenkel excitons are the excitons of organic semiconductors. They are constructed on highly localized atomic states. Their "Bohr radius", controlled by the atomic wave functions, is of the order of a single molecular block. This makes their binding energy as large as a fraction of e.V. or more.

Wannier excitons made of two fermions, the conduction electron and valence hole, were up to now commonly considered as elementary bosons, the possible fermion exchanges being included through effective scatterings, by lack of appropriate procedure. Over the last few years, we have developed this missing many-body theory [3, 4], through a procedure which allows us to treat the composite nature of Wannier excitons exactly. This theory now has its specific diagrammatic representation in terms of "Shiva diagrams" [5] which not only allow to visualize the tricky N -body exchanges which exist in these systems but also to calculate them readily. This new many-body theory has been successfully applied to a variety of physical effects such as Faraday rotation [6] and oscillation [7], spin precession [8] and teleportation [9], polariton and exciton Bose-Einstein condensation [10]. In each of these effects, the composite nature of the excitons plays a key role; in particular this new theory allows us to show that the replacement of Wannier excitons by elementary bosons misses the correct detuning behavior of all nonlinear optical effects induced by nonabsorbed photons.

Since organic materials are of potential importance for new electronic devices, the proper handling of many-body effects with Frenkel excitons along a theory similar to the one we have developed for Wannier excitons, is of high current interest. For readers not aware of this new composite exciton many-body theory, its fundamental ideas are briefly explained in a short review paper [3]. More details can be found in an extended Physics Report [4] and the references it contains to more than 30 published works.

In order to tackle Frenkel excitons on a firm basis we have, in a previous paper [11], rederived the basic concept leading to these excitons, starting from first principles, i.e., a microscopic Hamiltonian written in first quantization, with electron and hole kinetic energies, electron-ion, electron-electron, and ion-ion Coulomb interactions (This ion-ion term, which does not affect the electron motion, makes the system at hand neutral, in this way insuring the convergence of the overall Coulomb contribution in the large sample limit). Through a grouping of terms appropriate to highly localized electron states - this grouping being different from the one leading to valence and conduction bands on which the Wannier excitons are constructed - we make appear the atomic states of each ion. When overlaps between

relevant atomic states of different ion sites are negligible, these states can be used as a one-body basis to rewrite the system Hamiltonian in second quantization. In a second step, we transform the ground and excited atomic creation operators into electron and hole creation operators. Among the various Coulomb terms which keep the number of electron-hole pairs constant, one is insuring the local neutrality of the excitations. The resulting set of lowest excited states, made of these locally neutral excitations, with one electron and one hole on the same site, are degenerate in the absence of Coulomb interaction between sites. We then introduce these intersite interactions. Among them, one is a transfer term which destroys one electron-hole pair on one site and recreates it on another site. This transfer term splits the degenerate subspace made of one-site excitations into linear combinations of these excitations which are nothing but the Frenkel exciton states.

Frenkel excitons, made of electron-hole pairs localized on all possible atomic sites, are composite bosons, definitely. Their many-body effects thus have to be handled with extreme care if we want to fully trust the obtained results. This is why it can appear as appropriate to construct for them a full-proof procedure similar to the one we have used for Wannier excitons [3, 4, 12, 13, 14], these Wannier excitons also being linear combinations of electrons and holes but in extended states - not in localized states as for Frenkel excitons. Actually, due to this high localization, we can be tempted to believe that carrier exchanges between Frenkel excitons should reduce to zero; so that these excitons should behave as elementary bosons. In the present work, we show that this idea is actually a very naïve one: Frenkel excitons do behave as elementary bosons for some quantities, but differ from them in other important respects, making their many-body physics not easy to guess. This is why the many-body theory we here propose is going to be highly valuable because it allows us to tackle many-body effects with Frenkel excitons in a fully secure way.

Before going further, let us point out one important difference between Wannier and Frenkel excitons: Wannier excitons are controlled by one length for both, the interaction and the extension of the relative motion wave function. This length is the Bohr radius induced by the screened Coulomb interaction between electron and hole and calculated with the effective masses of the conduction and valence bands. The situation for Frenkel excitons is far more complex. We could at first think that Frenkel excitons have two lengths: the atomic wave function extension for the electron-hole pair "relative motion" and the Bohr radius for Coulomb interaction. Actually, Frenkel excitons have not one but two relevant Coulomb interactions: one for direct Coulomb processes between sites; the other for indirect processes, this last interaction being the one responsible for the excitation transfer between sites. In addition, as the electrons and holes on which the Frenkel excitons are constructed are not free, the proper effective mass to use in a "Bohr radius" is a priori unclear. Finally, the tight-binding approximation underlying Frenkel exciton corresponds to reduce the atomic wave function extension to zero, so that the length associated to the electron-hole "relative motion" de facto disappears. Due to these intrinsic difficulties and the expected interplay between these various "physical lengths", the many-body physics of Frenkel excitons is going to be far more subtle than the one of Wannier excitons, controlled by one length only.

The goal of the present paper is to settle the basis for a composite boson many-body theory appropriate to these Frenkel excitons. Using the formalism presented in the present work, we are going, in the near future, to address to the calculation of various observables, such as the ground state energy of N Frenkel excitons, the scattering rate of such excitons, and the nonlinear susceptibility of materials with Frenkel excitons, the later problem being very important for applications. Possible extension of the present theory can be to include effects of interaction with the vibrational modes, e.g., disorder and exciton-phonon coupling. This can be done by adding the corresponding potential to the Frenkel exciton Hamiltonian.

The paper is organized as follows.

In Section II, we recall the main steps leading to Frenkel excitons, as derived in our first work on these excitons [11].

In Section III, we derive the "Pauli scatterings" for carrier exchange between two Frenkel excitons, starting from the "deviation-from-boson operator" of these excitons [12, 13].

In Section IV, we introduce Shiva diagrams for carrier exchanges and show their similarities with Shiva diagrams for Wannier excitons [5]. We also point out an intrinsic difficulty of these Frenkel exciton Shiva diagrams linked to the tight-binding approximation which makes atomic electron-hole states used to represent Frenkel excitons, not a clean complete basis for all electron-hole pair states.

In Section V, we use these Pauli scatterings to calculate some relevant scalar products, including the normalization factor $N!F_N$ for N identical Frenkel excitons. We find that, as for Wannier excitons [12, 15], F_N which plays a key role in all exciton many-body effects, decreases exponentially with N due to carrier exchanges between composite bosons. This F_N turns out to have an extremely simple compact form due to the fact that Frenkel excitons are characterized by one quantum number only, the center-of-mass momentum \mathbf{Q} , while Wannier excitons in addition have a relative motion index ν . This is going to greatly simplify all results on many-body effects linked to the composite nature of these particles. We also discuss the physical meaning of the relevant dimensionless parameter η which controls carrier exchanges between excitons. We show that, in spite of our first understanding in the case of Wannier excitons, this

key parameter for many-body effects is not linked to the spatial extension of the electron-hole relative motion wave function but to the total number of excitons the sample can accommodate - otherwise η would reduce to zero in the case of Frenkel excitons. *This new physical understanding of η is one of the important results of the present work; it provides a significant step toward mastering the many-body physics of composite bosons, in general.*

In Section VI, we derive the closure relation which exists for N exciton states and we show that, while the prefactor for Wannier excitons [16] is $(1/N!)^2$, the prefactor for Frenkel excitons is $1/N!$ as for N elementary bosons. The fact that the prefactor for closure relation of composite bosons made of 2 fermions is not always $(1/N!)^2$, as we found for Wannier excitons, is also one of the important results of the paper. More on this prefactor can be found in Ref. [17].

In Section VII, we calculate the creation potential of one Frenkel exciton, as necessary to properly describe the Coulomb interaction of this exciton with the rest of the system [13, 14]. This Frenkel exciton creation potential actually splits into three conceptually different terms: One term comes from direct and exchange Coulomb processes inside the same site responsible for local neutrality; the second term originates from the indirect Coulomb processes between sites responsible for the excitation transfer; the third term comes from direct Coulomb processes between sites, this last contribution being similar to the one found for Wannier excitons.

In Section VIII, we calculate the interaction scatterings associated to the three parts of the creation potential. We find that the one associated to direct Coulomb processes between sites depends on the momentum transfer between the "in" and "out" excitons, as in the case of Wannier excitons [13, 14]. The scattering associated to the neutrality term is physically very strange as it does not depend on the momenta of the "in" and "out" excitons involved in the scattering. It however disappears from the physics of these excitons, when summation over all possible processes is performed. The third scattering, associated to the excitation transfer between sites, can also be seen as strange as it does not depend on the momentum transfer but just on the momenta of the "out" excitons. This is physically linked to the fact that the excitation transfer does not induce any momentum change. This third scattering actually corresponds to a "transfer assisted exchange": the coupling between two excitons comes from carrier exchange through a Pauli scattering while the energy-like contribution to this scattering comes from the transfer part of the Frenkel exciton energy resulting from indirect Coulomb processes. It can be of interest to note that this transfer assisted exchange scattering, somehow unexpected at first, has similarity with the "photon assisted exchange scattering" between two polaritons we recently identified [18]. The symmetry between "out" and "in" states is actually restored when considering energy conserving process, the scatterings being then equal, as shown in Section IX. In this Section VIII, we also calculate the Coulomb exchange scatterings when Coulomb interaction is followed by carrier exchange. We show that, as a consequence of the tight-binding approximation, the Coulomb exchange scatterings associated to direct and transfer processes reduce to zero.

To enlighten the interplay between the Pauli scattering and the various interaction scatterings between two Frenkel excitons, Section IX is devoted as an exercise to the calculation of the matrix element of the Frenkel exciton Hamiltonian in the two-exciton subspace. We make clear the part coming from non-interacting elementary bosons, the part coming from non-interacting composite excitons and the part coming from interaction between these excitons. We also compare this matrix element with the one obtained by assuming that Frenkel excitons are interacting elementary bosons. We again show that, in order to have equality between matrix elements for composite and bosonized Frenkel excitons, we are forced to use physically unacceptable effective scatterings, i.e., scatterings which would induce non-hermiticity in the Hamiltonian.

In Section X, we discuss the various results obtained on Frenkel excitons by comparing them with similar results obtained for elementary bosons and for Wannier excitons. We show that Frenkel excitons have similarities with both. This in particular means that they definitely differ from elementary bosons by various means which makes all intuitive handling of these excitons rather dangerous.

Section XI is a brief state-of-the-art. We discuss the approaches proposed by the two main groups who have tackled interaction between Frenkel excitons [19, 20, 21, 22, 23, 24, 25, 26] and point out some of the advantages of the present theory.

In the last Section, we conclude with a brief summary of the main results derived in the present work.

This paper is definitely quite long: We have chosen to include all fundamental results on the composite boson many-body theory for Frenkel excitons in a unique paper, for the reader to have at hand all the necessary tools to securely tackle any physical effect dealing with these excitons. Results on the Pauli and interaction scatterings [13, 14], the normalization factor [12, 15], the closure relation [16] and the Shiva diagram expansion [5] were the purposes of different papers at the time we were constructing a similar composite boson many-body theory for Wannier excitons. Through all these works, we have however learned what should be done to be fast and efficient; This is why we can now propose a rather compact presentation for all these important pieces of the composite Frenkel exciton puzzle.

II. ALL THE WAY TO FRENKEL EXCITONS

A. Electron and hole creation operators

Let us call $a_n^\dagger = a_{\nu=1, n}^\dagger$ the operator which creates one electron in the atomic excited state $\nu = 1$ on site n with n running from 1 to the total number N_s of sites in the periodic lattice. In the same way, the hole creation operator $b_n^\dagger = a_{\nu=0, n}$ destroys one electron in the atomic ground state $\nu = 0$ on site n . In the tight-binding limit in which the products of atomic wave functions are such that $\varphi_{\nu'}^*(\mathbf{r} - \mathbf{R}_{n'})\varphi_\nu(\mathbf{r} - \mathbf{R}_n) \simeq 0$ for all $n' \neq n$ when $(\nu, \nu') = (0, 1)$, these operators obey

$$a_{n'}a_n^\dagger + a_n^\dagger a_{n'} = \{a_{n'}, a_n^\dagger\} \simeq \delta_{n'n} \simeq \{b_{n'}, b_n^\dagger\} \quad (2.1)$$

$$\{a_{n'}, a_n\} = \{b_{n'}, b_n\} = \{a_{n'}, b_n^\dagger\} = 0 \simeq \{a_{n'}, b_n\} \quad (2.2)$$

They can thus be used as a one-body basis for electrons and holes in problems in which only the ground and first excited atomic states play a role.

B. Electron-hole Hamiltonian

The Hamiltonian for these free electrons and holes reads

$$H_{eh} = \varepsilon_e \sum_n a_n^\dagger a_n + \varepsilon_h \sum_n b_n^\dagger b_n \quad (2.3)$$

where the electron and hole energies ε_e and ε_h are slightly different from the excited and ground state atomic energies due to Coulomb interactions with the "jellium" made of one electron in the atomic ground state of each site n . A similar difference also exists for Wannier excitons, the electron and hole energies being slightly different from the conduction and valence electron energies.

The one-electron-hole-pair eigenstates of H_{eh} are $a_{n_e}^\dagger b_{n_h}^\dagger |v\rangle$ (see Fig. 1(a)), their energy being $\varepsilon_e + \varepsilon_h$. Since n_e and n_h can run from 1 to N_s , these states form a N_s^2 degenerate subspace.

C. Pair Hamiltonian

If we now take into account the *intrasite* direct and exchange contribution of the Coulomb potential, the resulting pair Hamiltonian is given by

$$H_{pair} = H_{eh} + V_{intra}$$

$$V_{intra} = -\varepsilon_0 \sum_n a_n^\dagger b_n^\dagger b_n a_n = -\varepsilon_0 \sum_n B_n^\dagger B_n \quad (2.4)$$

where $B_n^\dagger = a_n^\dagger b_n^\dagger$ creates one electron-hole pair on site n . The energy ε_0 gained by such a pair reads as

$$\varepsilon_0 = V_{\mathbf{R}=\mathbf{0}} \begin{pmatrix} 1 & 1 \\ 0 & 0 \end{pmatrix} - V_{\mathbf{R}=\mathbf{0}} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (2.5)$$

The Coulomb couplings between atomic states $V_{\mathbf{R}} \begin{pmatrix} \nu'_2 & \nu_2 \\ \nu'_1 & \nu_1 \end{pmatrix}$ correspond to atom on site n_1 , going from ν_1 to ν'_1 , while atom on site n_2 goes from ν_2 to ν'_2 , the two sites being at $\mathbf{R}_n = \mathbf{R}_{n_1} - \mathbf{R}_{n_2}$. It is related to the ground and first excited atomic wave functions $\varphi_\nu(\mathbf{r})$ through

$$V_{\mathbf{R}} \begin{pmatrix} \nu'_2 & \nu_2 \\ \nu'_1 & \nu_1 \end{pmatrix} = \int d\mathbf{r}_1 d\mathbf{r}_2 \varphi_{\nu'_1}^*(\mathbf{r}_1) \varphi_{\nu'_2}^*(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{R}|} \varphi_{\nu_2}(\mathbf{r}_2) \varphi_{\nu_1}(\mathbf{r}_1) \quad (2.6)$$

Note that Eq. (2.6) makes the two terms of ε_0 real while the orthogonality of atomic states makes it positive; so that V_{intra} forces local neutrality in the electron-hole excitation - as physically expected due to the electrostatic energy cost to separate electron from hole.

Consequently, among the N_s^2 one-pair states $a_{n_e}^\dagger b_{n_h}^\dagger |v\rangle$, the N_s states with the electron and hole on the same site have the same lowest energy (see Fig. 1 (b)). This leads to

$$(H_{pair} - E_{pair}) |n\rangle = 0 \quad (2.7)$$

$$|n\rangle = a_n^\dagger b_n^\dagger |v\rangle = B_n^\dagger |v\rangle \quad (2.8)$$

where $E_{pair} = \varepsilon_e + \varepsilon_h - \varepsilon_0$. Note that, since $a_n^2 = 0$, due to Eq. (2.2), the electron-hole operators B_n are such that

$$B_n^2 = 0 \quad (2.9)$$

D. Free exciton Hamiltonian

The next step is to introduce the "electron-hole exchange" part of the Coulomb interaction, i.e., the so-called "transfer term". It describes *intersite indirect* Coulomb processes between $\nu = 0$ and $\nu = 1$ states and allows excitation transfer between sites (see Fig. 1(c)). This leads to the "free exciton Hamiltonian" defined as

$$\begin{aligned} H_X^{(0)} &= H_{pair} + V_{transf} \\ V_{transf} &= \sum_{n_1 \neq n_2} V_{\mathbf{R}_{n_1} - \mathbf{R}_{n_2}} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} a_{n_1}^\dagger b_{n_1}^\dagger b_{n_2} a_{n_2} \\ &= \sum_{n_1 \neq n_2} V_{\mathbf{R}_{n_1} - \mathbf{R}_{n_2}} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} B_{n_1}^\dagger B_{n_2} \end{aligned} \quad (2.10)$$

The prefactor of this transfer term corresponds to Coulomb process in which one electron-hole pair on site n_2 recombines, i.e., the atom on site n_2 is deexcited from $\nu = 1$ to $\nu = 0$, while the atom on site n_1 is excited from $\nu = 0$ to $\nu = 1$. This transfer term splits the N_s degenerate subspace made of states $|n\rangle$ into N_s Frenkel exciton states defined as

$$|X_{\mathbf{Q}}\rangle = B_{\mathbf{Q}}^\dagger |v\rangle = \frac{1}{\sqrt{N_s}} \sum_{n=1}^{N_s} e^{i\mathbf{Q} \cdot \mathbf{R}_n} |n\rangle \quad (2.11)$$

While $|n\rangle$ corresponds to a localized excitation, Frenkel excitons $|X_{\mathbf{Q}}\rangle$ correspond to delocalized excitations through the sum over the \mathbf{R}_n sites it contains. By noting that

$$\begin{aligned} V_{transf} |X_{\mathbf{Q}}\rangle &= \frac{1}{\sqrt{N_s}} \sum_{n \neq m} \sum V_{\mathbf{R}_n - \mathbf{R}_m} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} e^{i\mathbf{Q} \cdot \mathbf{R}_m} a_n^\dagger b_n^\dagger |v\rangle \\ &= \frac{1}{\sqrt{N_s}} \sum_n e^{i\mathbf{Q} \cdot \mathbf{R}_n} a_n^\dagger b_n^\dagger |v\rangle \sum_{m \neq n} e^{-i\mathbf{Q} \cdot (\mathbf{R}_n - \mathbf{R}_m)} V_{\mathbf{R}_n - \mathbf{R}_m} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \end{aligned} \quad (2.12)$$

while the sum over m is independent on n due to translational invariance, we readily see that the $|X_{\mathbf{Q}}\rangle$ states are such that

$$(H_X^{(0)} - E_{\mathbf{Q}}) |X_{\mathbf{Q}}\rangle = 0 \quad (2.13)$$

where the exciton energy $E_{\mathbf{Q}}$ is related to the transfer coupling through

$$E_{\mathbf{Q}} = \varepsilon_e + \varepsilon_h - \varepsilon_0 + \mathcal{V}_{\mathbf{Q}} \quad (2.14)$$

$$\mathcal{V}_{\mathbf{Q}} = \sum_{\mathbf{R} \neq 0} e^{-i\mathbf{Q} \cdot \mathbf{R}} V_{\mathbf{R}} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \mathcal{V}_{\mathbf{Q}}^* \quad (2.15)$$

Note that $\mathcal{V}_{\mathbf{Q}}$ is real as expected for an energy since, due to Eq. (2.6), we do have

$$V_{\mathbf{R}}^* \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = V_{\mathbf{R}} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = V_{-\mathbf{R}} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (2.16)$$

Also note that there is a plus sign in the exponential of the Frenkel exciton creation operator while there is a minus sign in the exponential of the Frenkel exciton energy.

While Wannier excitons are characterized by a center of mass momentum \mathbf{Q} and a relative motion index, Frenkel excitons are characterized by \mathbf{Q} only. This is going to make the many-body physics of Frenkel excitons far simpler than the one of Wannier excitons, the "in" excitons ($\mathbf{Q}_1, \mathbf{Q}_2$) and the "out" excitons ($\mathbf{Q}'_1, \mathbf{Q}'_2$) of a scattering process being simply linked by $\mathbf{Q}'_1 + \mathbf{Q}'_2 = \mathbf{Q}_1 + \mathbf{Q}_2$, due to momentum conservation, without any additional degree of freedom.

By noting that the creation of an exciton \mathbf{Q} and the creation of an excitation on site n are linked by

$$B_{\mathbf{Q}}^{\dagger} = \frac{1}{\sqrt{N_s}} \sum_{n=1}^{N_s} e^{i\mathbf{Q} \cdot \mathbf{R}_n} B_n^{\dagger} \quad (2.17)$$

$$B_n^{\dagger} = a_n^{\dagger} b_n^{\dagger} = \frac{1}{\sqrt{N_s}} \sum_{\mathbf{Q}} e^{-i\mathbf{Q} \cdot \mathbf{R}_n} B_{\mathbf{Q}}^{\dagger} \quad (2.18)$$

while due to the lattice periodicity, we do have

$$\sum_{\mathbf{Q}} e^{i\mathbf{Q} \cdot (\mathbf{R}_{n'} - \mathbf{R}_n)} = N_s \delta_{n'n} \quad (2.19)$$

$$\sum_n e^{i(\mathbf{Q}' - \mathbf{Q}) \cdot \mathbf{R}_n} = N_s \delta_{\mathbf{Q}' \mathbf{Q}} \quad (2.20)$$

it is easy to show that the neutrality term V_{intra} in Eq. (2.4) reads as $-\varepsilon_0 \sum_{\mathbf{Q}} B_{\mathbf{Q}}^{\dagger} B_{\mathbf{Q}}$ while the transfer term V_{trans} reads as $\sum_{\mathbf{Q}} \mathcal{V}_{\mathbf{Q}} B_{\mathbf{Q}}^{\dagger} B_{\mathbf{Q}}$. Consequently, the free exciton Hamiltonian can be written as

$$H_X^{(0)} = \varepsilon_e \sum_n a_n^{\dagger} a_n + \varepsilon_h \sum_n b_n^{\dagger} b_n + S_X \quad (2.21)$$

$$S_X = \sum_{\mathbf{Q}} \zeta_{\mathbf{Q}} B_{\mathbf{Q}}^{\dagger} B_{\mathbf{Q}} \quad (2.22)$$

where we have set

$$\zeta_{\mathbf{Q}} = \mathcal{V}_{\mathbf{Q}} - \varepsilon_0 \quad (2.23)$$

Note that, while exciton operators can be used to rewrite the Coulomb part S_X of this free exciton Hamiltonian, this is not possible for the kinetic energy parts which still reads in terms of fermion operators. Also note that, although coming from two-body Coulomb interaction, S_X appears as a *diagonal* operator in the Frenkel exciton subspace. This is going to have important consequence for the scattering of two Frenkel excitons associated to this part of the Hamiltonian.

E. Interacting exciton Hamiltonian

Coulomb interaction also contains *intersite direct* contributions coming from electron-electron and hole-hole Coulomb interactions, as well as terms coming from direct electron-hole Coulomb processes, the exchange electron-hole term between sites being already included in $H_X^{(0)}$ through V_{transf} . Consequently, the interacting exciton Hamiltonian ultimately reads as

$$H_X = H_X^{(0)} + V_{coul} \quad (2.24)$$

$$V_{coul} = V_{ee} + V_{hh} + V_{eh}^{(dir)} \quad (2.25)$$

where the three terms of the Coulomb interaction between electrons and holes, shown in Fig. 1 (d, e, f), correspond to direct processes. They precisely read

$$V_{ee} = \frac{1}{2} \sum_{n_1 \neq n_2} V_{R_{n_1} - R_{n_2}} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} a_{n_1}^\dagger a_{n_2}^\dagger a_{n_2} a_{n_1} \quad (2.26)$$

$$V_{hh} = \frac{1}{2} \sum_{n_1 \neq n_2} V_{R_{n_1} - R_{n_2}} \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} b_{n_1}^\dagger b_{n_2}^\dagger b_{n_2} b_{n_1} \quad (2.27)$$

$$V_{eh}^{(dir)} = - \sum_{n_1 \neq n_2} V_{R_{n_1} - R_{n_2}} \begin{pmatrix} 1 & 1 \\ 0 & 0 \end{pmatrix} b_{n_1}^\dagger a_{n_2}^\dagger a_{n_2} b_{n_1} \quad (2.28)$$

Note that none of these three potentials can be exactly written in terms of exciton operators $B_{\mathbf{Q}}^\dagger$. Also note that the potential V_{coul} plays a role on states having more than one electron-hole pair since it contains operators acting on different sites, while each site can be occupied by one electron-hole pair only - in the absence of spin degrees of freedom. The introduction of these spin degrees of freedom and the quite subtle polarization effects they induce, are out of the scope of the present paper.

III. CARRIER EXCHANGES

A. Free pair operators

In the previous section, we made appear the excitations of one electron-hole pair on site n through the creation operators $B_n^\dagger = a_n^\dagger b_n^\dagger$ (see Eq. (2.8)). From Eqs. (2.1, 2), it is easy to show that the commutators of these free pair operators are such that

$$B_{n'} B_n - B_n B_{n'} = [B_{n'}, B_n] = 0 \quad (3.1)$$

$$[B_{n'}, B_n^\dagger]_- = \delta_{n'n} - D_{n'n} \quad (3.2)$$

where the deviation-from-boson operator $D_{n'n}$ for free pairs is given by

$$D_{n'n} = \delta_{n'n} (a_n^\dagger a_n + b_n^\dagger b_n) \quad (3.3)$$

Its commutator with another pair thus reduces to

$$[D_{n'n}, B_m^\dagger] = 2\delta_{n'n} \delta_{nm} B_m^\dagger \quad (3.4)$$

This quite simple result physically comes from the fact that electrons and holes have highly localized atomic wave functions; so that electron-hole pairs can feel each other by the Pauli exclusion principle when they are on the same site only.

B. Pauli scatterings for Frenkel excitons

Let us now turn to delocalized excitations, i.e., Frenkel excitons with creation operators given in terms of free pair operators by Eq. (2.17). From the commutators of these free pairs, we readily find

$$[B_{\mathbf{Q}'}, B_{\mathbf{Q}}] = 0 \quad (3.5)$$

$$[B_{\mathbf{Q}'}, B_{\mathbf{Q}}^\dagger] = \delta_{\mathbf{Q}'\mathbf{Q}} - D_{\mathbf{Q}'\mathbf{Q}} \quad (3.6)$$

where the deviation-from-boson operator for Frenkel excitons is given by

$$D_{\mathbf{Q}'\mathbf{Q}} = \Delta_{\mathbf{Q}-\mathbf{Q}'}^{(e)} + \Delta_{\mathbf{Q}-\mathbf{Q}'}^{(h)} \quad (3.7)$$

in which we have set

$$\Delta_{\mathbf{P}}^{(e)} = \frac{1}{N_s} \sum_n e^{i\mathbf{P} \cdot \mathbf{R}_n} a_n^\dagger a_n \quad (3.8)$$

and similarly for $\Delta_{\mathbf{P}}^{(h)}$ with $a_n^\dagger a_n$ replaced by $b_n^\dagger b_n$.

Using the expression of free pair operators B_n^\dagger in terms of Frenkel exciton operators given in Eq. (2.18) and the system periodicity through Eqs. (2.19, 20), it is easy to show that

$$\left[D_{\mathbf{Q}'\mathbf{Q}}, B_{\mathbf{P}}^\dagger \right]_- = \frac{2}{N_s} B_{\mathbf{P}+\mathbf{Q}-\mathbf{Q}'}^\dagger \quad (3.9)$$

If we now compare this equation with the standard definition of the Pauli scattering, deduced from the one for Wannier excitons, namely

$$\left[D_{\mathbf{Q}'\mathbf{Q}}, B_{\mathbf{P}}^\dagger \right]_- = \sum_{\mathbf{P}'} \left\{ \lambda \left(\begin{smallmatrix} \mathbf{Q}' & \mathbf{Q} \\ \mathbf{P}' & \mathbf{P} \end{smallmatrix} \right) + \lambda \left(\begin{smallmatrix} \mathbf{P}' & \mathbf{Q} \\ \mathbf{Q}' & \mathbf{P} \end{smallmatrix} \right) \right\} B_{\mathbf{P}'}^\dagger \quad (3.10)$$

we are led to identify the Pauli scattering of two Frenkel excitons with

$$\lambda \left(\begin{smallmatrix} \mathbf{Q}' & \mathbf{Q} \\ \mathbf{P}' & \mathbf{P} \end{smallmatrix} \right) = \lambda \left(\begin{smallmatrix} \mathbf{P}' & \mathbf{Q} \\ \mathbf{Q}' & \mathbf{P} \end{smallmatrix} \right) = \frac{1}{N_s} \delta_{\mathbf{P}'+\mathbf{Q}', \mathbf{P}+\mathbf{Q}} \quad (3.11)$$

When compared to the Pauli scatterings of Wannier excitons [13, 14], the one for Frenkel excitons appears as structureless: It barely contains the momentum conservation expected for any scattering. This extremely simple form of Pauli scattering can be traced back to the lack of degrees of freedom in the electron-hole pairs on which Frenkel excitons are constructed. Indeed, electrons and holes are in the two lowest atomic states by construction, i.e., the states for which the tight-binding approximation is valid. These $|\nu = (0, 1), n\rangle$ states do not form a complete set for all electron-hole pairs but can be used as a basis for the Frenkel exciton relevant states. In contrast, Wannier excitons are constructed on all the extended electron-hole states \mathbf{k}_e and \mathbf{k}_h which have the same center-of-mass momentum $\mathbf{k}_e + \mathbf{k}_h = \mathbf{Q}$. In addition to the center-of-mass momentum \mathbf{Q} , Wannier excitons thus have a momentum \mathbf{p} for the relative motion of the electron and the hole in the exciton. This momentum \mathbf{p} is related to the electron and hole momenta on which Wannier exciton is made, through $\mathbf{k}_e = \mathbf{p} + \alpha_e \mathbf{Q}$ and $\mathbf{k}_h = -\mathbf{p} + \alpha_h \mathbf{Q}$ where $\alpha_e = 1 - \alpha_h = m_e/(m_e + m_h)$.

C. Many-body effects coming from carrier exchanges

As for Wannier excitons, in order to derive many-body effects induced by carrier exchanges between any number of Frenkel excitons in an easy way, it is necessary to construct commutators similar to the ones of Eqs. (3.6, 9), but for N excitons [15, 19]. They read

$$\left[D_{\mathbf{P}'\mathbf{P}}, B_{\mathbf{Q}}^{\dagger N} \right] = 2 \frac{N}{N_s} B_{\mathbf{Q}+\mathbf{P}-\mathbf{P}'}^\dagger B_{\mathbf{P}}^{\dagger N-1} \quad (3.12)$$

$$\left[B_{\mathbf{P}'}^\dagger, B_{\mathbf{Q}}^{\dagger N} \right] = N B_{\mathbf{Q}}^{\dagger N-1} (\delta_{\mathbf{P}'\mathbf{Q}} - D_{\mathbf{P}'\mathbf{Q}})$$

$$- \frac{N(N-1)}{N_s} B_{\mathbf{Q}}^{\dagger N-2} B_{2\mathbf{Q}-\mathbf{P}'}^\dagger \quad (3.13)$$

as easy to recover by iteration. These commutators are just the ones for Wannier excitons (see Eq. (5) in Ref. [15]) with the Pauli scattering replaced by its value for Frenkel excitons, namely $N_s^{-1} \delta_{\mathbf{Q}'+\mathbf{P}', \mathbf{Q}+\mathbf{P}}$.

IV. SHIVA DIAGRAMS

Shiva diagrams for carrier exchanges between Wannier excitons [5] have been shown to be extremely powerful. They not only allow to visualize all carrier exchanges which take place between excitons, but also to calculate the

physical effects these exchanges induce readily. This makes them as valuable for the many-body physics of composite bosons as the Feynman diagrams for the many-body physics of elementary quantum particles. This is why it can be of interest to settle similar Shiva diagrams for carrier exchanges between Frenkel excitons. However, as shown below, their intuitive handling turns out to be less obvious due to the fact that the $B_n^\dagger |v\rangle$ states on which Frenkel excitons are constructed, do not form a clean complete basis for *all* one-pair states - in contrast to the free conduction electron and valence hole states on which the Wannier excitons are constructed.

A. Pauli scattering for two Frenkel excitons

Although possibly surprising at first, the very simple Pauli scattering of Frenkel excitons found in Eq. (3.11) still has the same formal structure as the one for Wannier excitons [13, 14]. Indeed, by writing the wave function of one electron on site n as $\langle r | a_n^\dagger | v \rangle = \varphi_{\nu=1}(\mathbf{r} - \mathbf{R}_n)$ and the wave function of one hole on site n as $\langle r | b_n^\dagger | v \rangle = \varphi_{\nu=0}^*(\mathbf{r} - \mathbf{R}_n)$, where $\varphi_{\nu=0,1}$ are the atomic wave functions, the exciton \mathbf{Q} wave function reads as

$$\langle \mathbf{r}_h, \mathbf{r}_e | \mathbf{Q} \rangle = \Phi_{\mathbf{Q}}(e, h) = \frac{1}{\sqrt{N_s}} \sum_n e^{i\mathbf{Q} \cdot \mathbf{R}_n} \varphi_e(\mathbf{r}_e - \mathbf{R}_n) \varphi_h(\mathbf{r}_h - \mathbf{R}_n) \quad (4.1)$$

where we have set $\varphi_e = \varphi_{\nu=1}$ and $\varphi_h = \varphi_{\nu=0}^*$. If we now calculate the diagram corresponding to hole exchange between two excitons shown in Fig. 2(a), it reads in terms of the Frenkel exciton wave functions given in Eq. (4.1) as

$$\int d\{r\} \Phi_{\mathbf{P}'}^*(e_1, h_2) \Phi_{\mathbf{Q}'}^*(e_2, h_1) \Phi_{\mathbf{Q}}(e_2, h_2) \Phi_{\mathbf{P}}(e_1, h_1) \quad (4.2)$$

This quantity contains integrals like

$$\int d\mathbf{r}_e \varphi_e^*(\mathbf{r}_e - \mathbf{R}_{n'}) \varphi_e(\mathbf{r}_e - \mathbf{R}_n) \simeq \delta_{n'n} \quad (4.3)$$

for highly localized atomic states; so that, due to Eq. (2.20), the value of this fermion exchange diagram (4.2) reduces to

$$\frac{1}{N_s^2} \sum_n e^{i(-\mathbf{P}' - \mathbf{Q}' + \mathbf{P} + \mathbf{Q}) \cdot \mathbf{R}_n} = \frac{1}{N_s} \delta_{\mathbf{P}' + \mathbf{Q}', \mathbf{P} + \mathbf{Q}} \quad (4.4)$$

which is nothing but the value of the Pauli scattering $\lambda\left(\begin{smallmatrix} \mathbf{Q}' & \mathbf{Q} \\ \mathbf{P}' & \mathbf{P} \end{smallmatrix}\right)$ obtained in Eq. (3.11). Consequently, as for Wannier excitons, the Pauli scattering of two Frenkel excitons can be represented by the Shiva diagram for fermion exchange between two excitons, shown in Fig. 2(a). The unique (relevant) difference comes from the fact that, due to the lack of relative motion index, the Pauli scattering for Frenkel excitons is the same for an electron exchange or a hole exchange.

B. Carrier exchange between more than two excitons

If we now turn to the carrier exchange between three Frenkel excitons which corresponds to the Shiva diagram of Fig. 2(b) and we calculate it along the standard rules for Shiva diagrams [5], i.e., by just writing what we read on the diagram, we find using Eqs. (4.1, 3) and Eq. (2.20) that

$$\lambda\left(\begin{smallmatrix} \mathbf{Q}'_3 & \mathbf{Q}_3 \\ \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{smallmatrix}\right) = \int d\{r\} \Phi_{\mathbf{Q}'_1}^*(e_1, h_2) \Phi_{\mathbf{Q}'_2}^*(e_3, h_1) \Phi_{\mathbf{Q}'_3}^*(e_2, h_3)$$

$$\Phi_{\mathbf{Q}_1}(e_1, h_1) \Phi_{\mathbf{Q}_2}(e_2, h_2) \Phi_{\mathbf{Q}_3}(e_3, h_3)$$

$$= \frac{1}{N_s^2} \delta_{\mathbf{Q}'_1 + \mathbf{Q}'_2 + \mathbf{Q}'_3, \mathbf{Q}_1 + \mathbf{Q}_2 + \mathbf{Q}_3}$$

This result agrees with the decomposition of three-body exchange in terms of a succession of two-body exchanges shown in Fig. 2(b), namely

$$\lambda \begin{pmatrix} \mathbf{Q}'_3 & \mathbf{Q}_3 \\ \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix} = \sum_{\mathbf{P}} \lambda \begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_3 \\ \mathbf{Q}'_3 & \mathbf{P} \end{pmatrix} \lambda \begin{pmatrix} \mathbf{P} & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix} \quad (4.6)$$

It is easy to check that this is also true for the four-body exchange shown in Fig. 2(c). And so on... So that the Shiva diagram for carrier exchange between N excitons just corresponds to

$$\frac{1}{N_s^{N-1}} \delta_{\mathbf{Q}'_1 + \dots + \mathbf{Q}'_N, \mathbf{Q}_1 + \dots + \mathbf{Q}_N}$$

C. Difficulties with Frenkel excitons

In spite of the above results, such a very visual way to calculate Shiva diagrams between N excitons and their decomposition in terms of exchanges between two excitons, encounter a major problem when dealing with the double exchange shown in Fig. 2(d): Indeed, Frenkel excitons \mathbf{Q}'_1 and \mathbf{Q}_1 are clearly made with the same electron-hole pair (see Fig. 2(e)); so that we should find $\delta_{\mathbf{Q}'_1 \mathbf{Q}_1} \delta_{\mathbf{Q}'_2 \mathbf{Q}_2}$ as for Wannier excitons. In contrast, two Pauli scatterings between two Frenkel excitons give

$$\begin{aligned} \sum_{\mathbf{P}, \mathbf{P}'} \lambda \begin{pmatrix} \mathbf{Q}'_2 & \mathbf{P}' \\ \mathbf{Q}'_1 & \mathbf{P} \end{pmatrix} \lambda \begin{pmatrix} \mathbf{P}' & \mathbf{Q}_2 \\ \mathbf{P} & \mathbf{Q}_1 \end{pmatrix} &= \frac{1}{N_s^2} \sum_{\mathbf{P}, \mathbf{P}'} \delta_{\mathbf{Q}'_1 + \mathbf{Q}_2, \mathbf{P}' + \mathbf{P}} \delta_{\mathbf{P}' + \mathbf{P}, \mathbf{Q}_1 + \mathbf{Q}_2} \\ &= \frac{1}{N_s} \delta_{\mathbf{Q}'_1 + \mathbf{Q}_2, \mathbf{Q}_1 + \mathbf{Q}_2} \end{aligned} \quad (4.7)$$

which is nothing but the Pauli scattering $\lambda \begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix}$ and thus definitely different from an identity.

This problem must be associated to the fact that, while for Wannier excitons, the two possible ways to couple two electrons and two holes into two excitons leads to [12]

$$B_n^\dagger B_j^\dagger = - \sum_{m, n} \lambda \begin{pmatrix} n & j \\ m & i \end{pmatrix} B_m^\dagger B_n^\dagger \quad (4.8)$$

such a rearrangement is not possible for Frenkel excitons; so that a similar relation does not exist for them. Indeed, using Eq. (2.17), we do have

$$B_{\mathbf{P}}^\dagger B_{\mathbf{Q}}^\dagger = \frac{1}{N_s} \sum_n e^{i\mathbf{P} \cdot \mathbf{R}_n} e^{i\mathbf{Q} \cdot \mathbf{R}_{n'}} a_n^\dagger b_{n'}^\dagger a_{n'}^\dagger b_n^\dagger \quad (4.9)$$

Due to the tight-binding approximation, we cannot make an exciton out of the electron-hole operator $a_n^\dagger b_{n'}^\dagger$, except for $n' = n$, the product $a_n^\dagger b_n^\dagger a_{n'}^\dagger b_{n'}^\dagger$ then reducing to 0, according to Eq. (2.9).

The difficulty to rewrite $B_{\mathbf{Q}}^\dagger B_{\mathbf{Q}'}^\dagger$ in terms of two other Frenkel excitons, when compared to Wannier excitons, can be mathematically assigned to the fact that the free electron-hole pairs $a_{k_e}^\dagger b_{k_h}^\dagger |v\rangle$ form a clean complete basis for one electron and one hole while this is not true for the trapped pairs $a_n^\dagger b_n^\dagger |v\rangle$. As previously discussed, these states can be used as a basis in the tight-binding limit only, i.e., when the two lowest atomic (bound) states are the only relevant states of the problem. However, Eq. (4.8) as well as the identity between diagrams 2(d)-(f) for Wannier excitons, relies on an exact closure relation for all the *intermediate* electron-hole states on which the sums are taken while this closure relation using the two lowest atomic states is only approximate in the case of Frenkel excitons.

This may lead us to think that, since there is one way only to construct two Frenkel excitons out of two electron-hole pairs, many-body effects coming from fermion exchanges between Frenkel excitons which result from their composite nature, must be somehow suppressed. The situation is actually far more subtle, as shown in the next sections.

V. CALCULATION OF SOME RELEVANT SCALAR PRODUCTS

As for Wannier excitons, physical effects dealing with Frenkel excitons ultimately read in terms of scalar products of Frenkel exciton states. Let us now calculate a few of them along the line we have used for Wannier excitons [12, 19]. Due to the structureless form of the Pauli scattering, these scalar products turn out to be far simpler than the ones for Wannier excitons. This makes the Frenkel exciton many-body physics induced by carrier exchanges also far simpler.

A. Scalar product of two-exciton states

Using Eqs. (3.2,4), the scalar product of two-free-pair states reads as

$$\begin{aligned} \langle v | B_{n'_1} B_{n'_2} B_{n_2}^\dagger B_{n_1}^\dagger | v \rangle &= \langle v | B_{n'_1} \{ B_{n_2}^\dagger B_{n'_2} - \delta_{n'_2 n_2} - D_{n'_2 n_2} \} B_{n_1}^\dagger | v \rangle \\ &= \delta_{n'_1 n_1} \delta_{n'_2 n_2} + \delta_{n'_1 n_2} \delta_{n'_2 n_1} - 2\delta_{n'_1 n_1} \delta_{n'_2 n_2} \delta_{n'_1 n'_2} \end{aligned} \quad (5.1)$$

So that $\langle v | B_n B_{n'} B_n^\dagger B_n^\dagger | v \rangle = 1 - \delta_{n'n}$ reduces to 0 when $n' = n$ as expected since a given site cannot be occupied by two electrons in the absence of degeneracy. This shows that while there are N_s one-pair states $B_n^\dagger | v \rangle$, the number of different two-pair states $B_m^\dagger B_n^\dagger | v \rangle$ is $N_s(N_s - 1)/2$ since m must be different from n , while $B_n^\dagger B_m^\dagger = B_m^\dagger B_n^\dagger$.

If we now turn to two-exciton states, the same procedure leads, using Eqs. (3.6, 9), to

$$\langle v | B_{\mathbf{Q}'_1} B_{\mathbf{Q}'_2} B_{\mathbf{Q}_2}^\dagger B_{\mathbf{Q}_1}^\dagger | v \rangle = \delta_{\mathbf{Q}'_1 \mathbf{Q}_1} \delta_{\mathbf{Q}'_2 \mathbf{Q}_2} + \delta_{\mathbf{Q}'_1 \mathbf{Q}_2} \delta_{\mathbf{Q}'_2 \mathbf{Q}_1} - \frac{2}{N_s} \delta_{\mathbf{Q}'_1 + \mathbf{Q}'_2 \mathbf{Q}_1 + \mathbf{Q}_2} \quad (5.2)$$

By noting that the last term of the above bracket is nothing but $-\lambda \left(\frac{\mathbf{Q}'_2 \mathbf{Q}_2}{\mathbf{Q}'_1 \mathbf{Q}_1} \right) - \lambda \left(\frac{\mathbf{Q}'_1 \mathbf{Q}_2}{\mathbf{Q}'_2 \mathbf{Q}_1} \right)$, we see that this result which is shown in Fig. 3, is formally the same as the one for Wannier excitons, namely [12]

$$\langle v | B_m B_n B_i^\dagger B_j^\dagger | v \rangle = \delta_{mi} \delta_{nj} - \lambda \binom{n \ j}{m \ i} + (m \leftrightarrow n) \quad (5.3)$$

with (m, n, i, j) replaced by $(\mathbf{Q}'_1, \mathbf{Q}'_2, \mathbf{Q}_1, \mathbf{Q}_2)$.

It follows from Eq. (5.2) that the norm of two Frenkel exciton states

$$\langle v | B_{\mathbf{Q}_1} B_{\mathbf{Q}_2} B_{\mathbf{Q}_2}^\dagger B_{\mathbf{Q}_1}^\dagger | v \rangle = 1 + \delta_{\mathbf{Q}_1 \mathbf{Q}_2} - \frac{2}{N_s} \quad (5.4)$$

differs from 0 for $\mathbf{Q}_1 = \mathbf{Q}_2$; so that there are $N_s^2/2$ different two-exciton states $B_{\mathbf{Q}_1}^\dagger B_{\mathbf{Q}_2}^\dagger | v \rangle$ since $B_{\mathbf{Q}_1}^\dagger B_{\mathbf{Q}_2}^\dagger = B_{\mathbf{Q}_2}^\dagger B_{\mathbf{Q}_1}^\dagger$ while there only are $N_s(N_s - 1)/2$ different two-pair states $B_m^\dagger B_n^\dagger | v \rangle$. Consequently, as for Wannier excitons, the two-Frenkel exciton states form an overcomplete set [16].

Note that, while the overcompleteness of the two Wannier-exciton states readily follows from Eq. (5.3), we have shown that such a relation - which comes from the two ways to bind two free electrons and two free holes into two Wannier excitons - does not exist for Frenkel excitons due to the tight-binding approximation which is at the basis of the Frenkel exciton concept. Nevertheless, two-Frenkel-exciton states, like two-Wannier-exciton states, form an overcomplete set.

B. Scalar product of three-exciton states

If we now turn to the scalar product of three-exciton states shown in Fig. 4, we find using the commutators of Eqs. (3.6, 9)

$$\begin{aligned} \langle v | B_{\mathbf{Q}'_3} B_{\mathbf{Q}'_2} B_{\mathbf{Q}'_1} B_{\mathbf{Q}_1}^\dagger B_{\mathbf{Q}_2}^\dagger B_{\mathbf{Q}_3}^\dagger | v \rangle &= \{ \delta_{\mathbf{Q}'_1 \mathbf{Q}_1} \delta_{\mathbf{Q}'_2 \mathbf{Q}_2} \delta_{\mathbf{Q}'_3 \mathbf{Q}_3} + 5 \text{ perm.} \} \\ &\quad - \frac{2}{N_s} \{ \delta_{\mathbf{Q}'_1 + \mathbf{Q}'_2 \mathbf{Q}_1 + \mathbf{Q}_2} \delta_{\mathbf{Q}'_3 \mathbf{Q}_3} + 8 \text{ perm.} \} \\ &\quad + \frac{12}{N_s^2} \delta_{\mathbf{Q}'_1 + \mathbf{Q}'_2 + \mathbf{Q}'_3 \mathbf{Q}_1 + \mathbf{Q}_2 + \mathbf{Q}_3} \end{aligned} \quad (5.5)$$

This result agrees with the standard rules [5] for calculating scalar products through Shiva diagrams shown in Fig. 4, with the values of fermion exchanges between two and three Frenkel excitons, given in Eqs. (4.2, 4) and Eq. (4.5).

C. Scalar product of N identical exciton states

As for Wannier excitons, the normalization factor of N identical Frenkel excitons plays a crucial role in all physically relevant matrix elements involving N excitons, since most of them usually are in the same state. Let us write this normalization factor as [12, 15]

$$\langle v | B_{\mathbf{Q}}^N B_{\mathbf{Q}}^{\dagger N} | v \rangle = N! F_N \quad (5.6)$$

while $N!$ is the value this scalar product would have if Frenkel excitons were elementary bosons. We are going to show that, in contrast to Wannier excitons for which F_N depends on the state (ν, \mathbf{Q}) in which the N excitons are, F_N for Frenkel excitons depends on N but not on the exciton state considered, labelled by \mathbf{Q} . This property is going to greatly simplify all results on many-body effects with Frenkel excitons.

(i) Pedestrian way to calculate F_N

The pedestrian calculation of F_N relies on the commutator (3.10). While $\langle v | B_{\mathbf{Q}} B_{\mathbf{Q}}^{\dagger} | v \rangle = 1$ so that $F_1 = 1$, it is easy to show that

$$\begin{aligned} \langle v | B_{\mathbf{Q}}^2 B_{\mathbf{Q}}^{\dagger 2} | v \rangle &= 2 \left(1 - \frac{1}{N_s} \right) \\ \langle v | B_{\mathbf{Q}}^3 B_{\mathbf{Q}}^{\dagger 3} | v \rangle &= 3! \left(1 - \frac{1}{N_s} \right) \left(1 - \frac{2}{N_s} \right) \end{aligned} \quad (5.7)$$

and so on... This leads us to conclude that F_N should read as

$$F_N = \left(1 - \frac{1}{N_s} \right) \dots \left(1 - \frac{N-1}{N_s} \right) = \frac{N_s!}{(N_s - N)! N_s^N} \quad (5.8)$$

which makes F_N independent of the Frenkel exciton \mathbf{Q} considered, a result somewhat surprising at first.

(ii) More elaborate derivation

A more elaborate way to calculate F_N makes use of the recursion relation between the $\langle v | B_{\mathbf{Q}}^N B_{\mathbf{Q}}^{\dagger N} | v \rangle$ easy to obtain from Eq. (3.13). This equation leads to

$$\begin{aligned} \langle v | B_{\mathbf{Q}}^N B_{\mathbf{Q}}^{\dagger N} | v \rangle &\equiv \langle v | B_{\mathbf{Q}}^{N-1} B_{\mathbf{Q}} B_{\mathbf{Q}}^{\dagger N} | v \rangle \\ &= \left(N - \frac{N(N-1)}{N_s} \right) \langle v | B_{\mathbf{Q}}^{N-1} B_{\mathbf{Q}}^{\dagger N-1} | v \rangle \end{aligned} \quad (5.9)$$

So that

$$F_N = \left(1 - \frac{N-1}{N_s} \right) F_{N-1} \quad (5.10)$$

from which the expression of F_N given in Eq. (5.8) readily follows.

(iii) Recursion relation between the F_N 's

Even if F_N for Frenkel excitons has a nicely compact expression, it can be of interest to note that, due to Eq. (5.10), F_N can be written as a sum of all the other F_N 's according to

$$F_N = F_{N-1} - \frac{N-1}{N_s} F_{N-2} + \frac{(N-1)(N-2)}{N_s^2} F_{N-3} - \dots \quad (5.11)$$

This series just is the analog of the one for Wannier excitons, namely (see Eq. (15) Ref. [15])

$$F_N = \sum_{n=1}^N (-1)^{n-1} \frac{(N-1)!}{(N-n)!} \sigma_n F_{N-n} \quad (5.12)$$

where the σ_n 's are the Shiva diagrams for fermion exchanges with n excitons \mathbf{Q} on both sides. Indeed, as shown in Section IV, these Shiva diagrams in the case of Frenkel excitons reduce to $1/N_s^{n-1} \delta_{\mathbf{Q}'_1 + \dots + \mathbf{Q}'_n, \mathbf{Q}_1 + \dots + \mathbf{Q}_n}$, i.e., $1/N_s^{n-1}$ when all the \mathbf{Q} 's are equal.

(iv) Density expansion
From Eq. (5.10), we find

$$\frac{F_{N-1}}{F_N} = \frac{N_s}{N_s + 1 - N} \simeq 1 + O\left(\frac{N}{N_s}\right) \quad (5.13)$$

for $1 \ll N \ll N_s$. This result is again fully consistent with $F_{N-1}/F_N = 1 + O(\eta)$ as found for Wannier excitons [15] where $\eta = N(a_x/L)^D$ with N being the number of excitons at hand, a_x the exciton Bohr radius or relative motion wave function extension, L the sample size and D the space dimension. Indeed, the ratio of the sample volume L^D divided by the Wannier exciton volume a_x^D is nothing but the maximum number of excitons the sample can accept in the absence of spin degrees of freedom. This thus makes η for Wannier excitons equal to the ratio of the number of excitons at hand divided by the maximum possible number of excitons, this ratio being small in the dilute limit, i.e., when excitons exist. In the case of Frenkel excitons, it is clear that the maximum number of excitons has nothing to do with the Frenkel exciton relative motion extension because this extension reduces to zero in the tight binding limit. This maximum exciton number is just the number N_s of atomic sites; so that the small dimensionless parameter for these excitons, associated to their density, must be identified with

$$\eta = \frac{N}{N_s} \quad (5.14)$$

This expression leads us to reconsider the physical understanding of the parameter which controls carrier exchanges between composite bosons. While the spatial extension of the electron-hole relative motion wave function seemed at first to us a relevant length for the control of carrier exchanges, the expression of η we here find for Frenkel excitons shows that the physically relevant quantity for the low density expansion of carrier exchanges cannot be this length - otherwise η would reduce to zero in the tight-binding limit - but must be the maximum number of excitons we can put in the sample volume V . With this new understanding, it becomes easy to grasp why carrier exchanges are not totally suppressed in Frenkel exciton systems.

If we now come back to the exact value of F_N given in Eq. (5.8), we can show that, as for Wannier excitons, it decreases exponentially with $N\eta$. This is done by using the Stirling formula $p! \simeq p^p e^{-p} \sqrt{2\pi p}$ in Eq. (5.8). For N_s and $N_s - N$ both large, we find

$$F_N \simeq e^{-N} (1 - \eta)^{-N(\frac{1}{\eta}-1)} (1 - \eta)^{-1/2} \quad (5.15)$$

Since $a^b = e^{b \ln a}$, we then get when all the $N\eta$'s are small

$$F_N \simeq e^{-N(\frac{\eta}{2} + \frac{\eta^2}{6} + \dots)} \quad (5.16)$$

A similar exponential decrease is also found for Wannier excitons.

VI. CLOSURE RELATION FOR FRENKEL EXCITONS

We have shown that, due to the existence of a clean closure relation for the electrons and holes on which the Wannier excitons are constructed, these composite boson excitons have a nicely compact closure relation which reads [16]

$$I = \frac{1}{(N!)^2} \sum B_{i_1}^\dagger \dots B_{i_N}^\dagger |v\rangle \langle v| B_{i_N} \dots B_{i_1} \quad (6.1)$$

the closure relation for elementary bosons being just the same with $1/(N!)^2$ replaced by $1/N!$.

We are going to show that the situation for Frenkel excitons is rather different due to the tight-binding approximation underlying the Frenkel exciton concept.

A. One electron-hole pair / one Frenkel exciton

Starting from the closure relation for electrons in atomic site n

$$I = \sum a_n^\dagger |v\rangle \langle v| a_n \quad (6.2)$$

and the similar relation for holes, we can construct the closure relation for one-electron-hole pairs. It reads

$$\begin{aligned}
I &= \sum_n \sum_{n'} a_n^\dagger b_{n'}^\dagger |v\rangle \langle v| b_{n'} a_n \\
&= \sum_n B_n^\dagger |v\rangle \langle v| B_n + \sum_{n \neq n'} \sum a_n^\dagger b_{n'}^\dagger |v\rangle \langle v| b_{n'} a_n
\end{aligned} \tag{6.3}$$

Using Eqs. (2.18, 20), it is easy to show that the first sum can be rewritten as

$$\sum_{\mathbf{Q}'} B_{\mathbf{Q}'}^\dagger |v\rangle \langle v| B_{\mathbf{Q}} \frac{1}{N_s} \sum_n e^{i(\mathbf{Q}' - \mathbf{Q}) \cdot \mathbf{R}_n} = \sum_{\mathbf{Q}} B_{\mathbf{Q}}^\dagger |v\rangle \langle v| B_{\mathbf{Q}}$$

while the second sum of Eq. (6.3) can be dropped out since it corresponds to projections over states way off by an energy ε_0 , their electrons and holes being in different sites. Consequently, the closure relation for one-Frenkel exciton states can be approximated by

$$I \simeq \sum_{\mathbf{Q}} B_{\mathbf{Q}}^\dagger |v\rangle \langle v| B_{\mathbf{Q}} \tag{6.4}$$

B. Two free pairs / two Frenkel excitons

Let us now turn to two-pairs. The closure relation for two electrons reads

$$I = \frac{1}{2!} \sum a_{n_1}^\dagger a_{n_2}^\dagger |v\rangle \langle v| a_{n_2} a_{n_1} \tag{6.5}$$

and similarly for holes. By rewriting this hole closure relation as

$$\begin{aligned}
I &= \frac{1}{2!} \sum_{n'_2} \left\{ \sum_{n'_1=(n_1, n_2)} b_{n'_1}^\dagger b_{n'_2}^\dagger |v\rangle \langle v| b_{n'_2} b_{n'_1} \right. \\
&\quad \left. + \sum_{n'_1 \neq (n_1, n_2)} b_{n'_1}^\dagger b_{n'_2}^\dagger |v\rangle \langle v| b_{n'_2} b_{n'_1} \right\}
\end{aligned}$$

and by splitting the sum over n'_2 in the same way, we find that the closure relation for two electron-hole pairs restricted to the degenerate subspace having an energy $(\varepsilon_e + \varepsilon_h - \varepsilon_0)$ can be written as

$$\begin{aligned}
I &\simeq \left(\frac{1}{2!} \right)^2 2 \sum a_{n_1}^\dagger b_{n_1}^\dagger a_{n_2}^\dagger b_{n_2}^\dagger |v\rangle \langle v| b_{n_2} a_{n_2} b_{n_1} a_{n_1} \\
&= \frac{1}{2} \sum B_{n_1}^\dagger B_{n_2}^\dagger |v\rangle \langle v| B_{n_2} B_{n_1}
\end{aligned} \tag{6.6}$$

If we now rewrite free pairs in terms of Frenkel excitons according to Eq. (2.18) and we use Eq. (2.20), the above closure relation leads to

$$I \simeq \frac{1}{2!} \sum_{\mathbf{Q}_1 \mathbf{Q}_2} B_{\mathbf{Q}_1}^\dagger B_{\mathbf{Q}_2}^\dagger |v\rangle \langle v| B_{\mathbf{Q}_2} B_{\mathbf{Q}_1} \tag{6.7}$$

We see that this sum has the same prefactor $1/2!$ as the one for two elementary bosons. This equality between prefactors can be understood by noting that there is only one way to construct two Frenkel excitons out of two pairs belonging to the $(\varepsilon_e + \varepsilon_h - \varepsilon_0)$ subspace; so that these excitons behave as elementary bosons with respect to this projection operator.

C. Direct check

It is possible to check the validity of the approximate closure relation for two free pairs, given in Eq. (6.6), by inserting it in front of $B_{m_1}^\dagger B_{m_2}^\dagger |v\rangle$. Indeed Eq. (5.1) for the scalar product of two-free-pair states readily gives

$$\frac{1}{2} \sum B_{n_1}^\dagger B_{n_2}^\dagger |v\rangle \langle v| B_{n_2} B_{n_1} B_{m_1}^\dagger B_{m_2}^\dagger |v\rangle = B_{m_1}^\dagger B_{m_2}^\dagger |v\rangle \quad (6.8)$$

for any $m_1 \neq m_2$, as expected for a closure relation, the state $B_m^{\dagger 2} |v\rangle$ reducing to 0 since the same site cannot accommodate two electrons.

The check of the approximate closure relation for two Frenkel excitons, given in Eq. (6.7), is less trivial. Indeed, if we insert Eq. (6.7) in front of $B_{\mathbf{P}_1}^\dagger B_{\mathbf{P}_2}^\dagger |v\rangle$, we find, using Eq. (5.2) for the scalar product of two-Frenkel exciton states,

$$\begin{aligned} \frac{1}{2} \sum_{\mathbf{Q}_1 \mathbf{Q}_2} B_{\mathbf{Q}_1}^\dagger B_{\mathbf{Q}_2}^\dagger |v\rangle \langle v| B_{\mathbf{Q}_2} B_{\mathbf{Q}_1} B_{\mathbf{P}_1}^\dagger B_{\mathbf{P}_2}^\dagger |v\rangle &= B_{\mathbf{P}_1}^\dagger B_{\mathbf{P}_2}^\dagger |v\rangle \\ &- \sum_{\mathbf{Q}_1 \mathbf{Q}_2} \lambda \left(\begin{smallmatrix} \mathbf{Q}_2 & \mathbf{P}_2 \\ \mathbf{Q}_1 & \mathbf{P}_1 \end{smallmatrix} \right) B_{\mathbf{Q}_1}^\dagger B_{\mathbf{Q}_2}^\dagger |v\rangle \end{aligned} \quad (6.9)$$

In order to show that the above sum reduces to zero as necessary to prove that Eq. (6.7) is indeed a closure relation, we use Eq. (3.11) for $\lambda \left(\begin{smallmatrix} \mathbf{Q}_2 & \mathbf{P}_2 \\ \mathbf{Q}_1 & \mathbf{P}_1 \end{smallmatrix} \right)$. We find

$$\sum_{\mathbf{Q}_1 \mathbf{Q}_2} \lambda \left(\begin{smallmatrix} \mathbf{Q}_2 & \mathbf{P}_2 \\ \mathbf{Q}_1 & \mathbf{P}_1 \end{smallmatrix} \right) B_{\mathbf{Q}_1}^\dagger B_{\mathbf{Q}_2}^\dagger = \frac{1}{N_s} \sum_{\mathbf{Q}} B_{\mathbf{P}_1+\mathbf{Q}}^\dagger B_{\mathbf{P}_2-\mathbf{Q}}^\dagger |v\rangle \quad (6.10)$$

We then rewrite exciton operators in terms of free pairs according to Eq. (2.17) and we use Eq. (2.19). This leads to

$$\begin{aligned} \sum_{\mathbf{Q}} B_{\mathbf{P}_1+\mathbf{Q}}^\dagger B_{\mathbf{P}_2-\mathbf{Q}}^\dagger &= \sum_{n_1 n_2} e^{i(\mathbf{P}_1 \cdot \mathbf{R}_{n_1} + \mathbf{P}_2 \cdot \mathbf{R}_{n_2})} B_{n_1}^\dagger B_{n_2}^\dagger \sum_{\mathbf{Q}} e^{i\mathbf{Q} \cdot (\mathbf{R}_{n_1} - \mathbf{R}_{n_2})} \\ &= N_s \sum_{n_1} e^{i(\mathbf{P}_1 - \mathbf{P}_2) \cdot \mathbf{R}_{n_1}} B_{n_1}^{\dagger 2} \end{aligned} \quad (6.11)$$

So that since, $B_n^2 = 0$, due to Eq. (2.9), we end with

$$\sum_{\mathbf{Q}_1 \mathbf{Q}_2} \lambda \left(\begin{smallmatrix} \mathbf{Q}_2 & \mathbf{P}_2 \\ \mathbf{Q}_1 & \mathbf{P}_1 \end{smallmatrix} \right) B_{\mathbf{Q}_1}^\dagger B_{\mathbf{Q}_2}^\dagger = 0 \quad (6.12)$$

This result must be physically related to the fact that there is only one way to write two Frenkel excitons out of two pairs: If we try to exchange the carriers of two Frenkel excitons as in the sum (6.12), we get zero.

D. Closure relation for N Frenkel excitons

A similar procedure performed for N pairs leads to an approximate closure relation for N Frenkel excitons which reads

$$I \simeq \frac{1}{N!} \sum B_{\mathbf{Q}_1}^\dagger \dots B_{\mathbf{Q}_N}^\dagger |v\rangle \langle v| B_{\mathbf{Q}_N} \dots B_{\mathbf{Q}_1} \quad (6.13)$$

with again the same $1/N!$ prefactor as the one for N elementary bosons.

VII. CREATION POTENTIAL FOR FRENKEL EXCITONS

Frenkel excitons feel each other through exchanges as described in the previous sections. This "interaction", generated by the Pauli exclusion principle, is of course unusual in the sense that it gives rise to dimensionless Pauli scatterings as shown in Section III. Frenkel excitons also interact through the Coulomb potential which exists between their fermionic components. As for Wannier excitons [13], there is no clean way to write Coulomb interactions between two excitons as a potential due to the composite nature of the particles. Here also, we are going to overcome this difficulty by introducing a set of "creation potentials". From them, it becomes formally possible to derive the interaction scatterings of two Frenkel excitons, as we shown in the next section.

A. Definition

The creation potential $V_{\mathbf{Q}}^\dagger$ of the Frenkel exciton \mathbf{Q} is defined through

$$\left[H_X, B_{\mathbf{Q}}^\dagger \right] = E_{\mathbf{Q}} B_{\mathbf{Q}}^\dagger + V_{\mathbf{Q}}^\dagger \quad (7.1)$$

where $H_X = H_X^{(0)} + V_{coul}$ is the interacting exciton Hamiltonian defined in Eq. (2.24) while $H_X^{(0)} = H_{eh} + S_X$ with H_{eh} , S_X and V_{coul} given by Eqs. (2.3, 22, 25). To get $V_{\mathbf{Q}}^\dagger$ we have to calculate the commutator of the Frenkel exciton creation operator $B_{\mathbf{Q}}^\dagger$ with each of the three terms of H_X . However, since $(H_X^{(0)} - E_{\mathbf{Q}}) B_{\mathbf{Q}}^\dagger |v\rangle = 0$, the $E_{\mathbf{Q}} B_{\mathbf{Q}}^\dagger$ part in the RHS of Eq. (7.1) must come from $[H_X^{(0)}, B_{\mathbf{Q}}^\dagger]$. This leads us to split Eq. (7.1) as

$$\left[H_X^{(0)}, B_{\mathbf{Q}}^\dagger \right] = E_{\mathbf{Q}} B_{\mathbf{Q}}^\dagger + S_{\mathbf{Q}}^\dagger \quad (7.2)$$

$$\left[V_{coul}, B_{\mathbf{Q}}^\dagger \right] = W_{\mathbf{Q}}^\dagger \quad (7.3)$$

The Frenkel exciton creation potential is thus going to appear as

$$V_{\mathbf{Q}}^\dagger = S_{\mathbf{Q}}^\dagger + W_{\mathbf{Q}}^\dagger \quad (7.4)$$

these two parts being conceptually quite different: $W_{\mathbf{Q}}^\dagger$ associated to V_{coul} comes from direct Coulomb processes between sites. It has similarity with the Wannier exciton creation potential. In contrast, $S_{\mathbf{Q}}^\dagger$, which originates from S_X , essentially comes from indirect Coulomb processes; these processes, crucial for Frenkel excitons as they are responsible for the excitation transfer, are usually neglected for Wannier excitons. They precisely correspond to the so-called "electron-hole exchange".

B. Free exciton creation potential

The free exciton Hamiltonian $H_X^{(0)}$ contains an electron - hole kinetic energy term H_{eh} defined in Eq. (2.3). Its commutator with $B_{\mathbf{Q}}^\dagger$ readily gives

$$\begin{aligned} \left[H_{eh}, B_{\mathbf{Q}}^\dagger \right] &= \left[\varepsilon_e \sum a_n^\dagger a_n + \varepsilon_h \sum b_n^\dagger b_n, \sum \frac{e^{i\mathbf{Q} \cdot \mathbf{R}_m}}{\sqrt{N_s}} a_m^\dagger b_m^\dagger \right] \\ &= (\varepsilon_e + \varepsilon_h) B_{\mathbf{Q}}^\dagger \end{aligned} \quad (7.5)$$

$H_X^{(0)}$ also contains Coulomb contributions through S_X . Although S_X reads as a *one*-body diagonal potential in the Frenkel exciton subspace, it can produce interactions between *two* excitons through the carrier exchanges the exciton composite nature allows - an idea not trivial at first.

By using Eq. (3.6), it is straightforward to see that $[S_X, B_Q^\dagger]$ reads in terms of the deviation-from-boson operator for Frenkel exciton as

$$\begin{aligned} [S_X, B_Q^\dagger] &= \left[\sum_{Q'} \zeta_{Q'} B_{Q'}^\dagger B_{Q'}, B_Q^\dagger \right] = \sum_{Q'} \zeta_{Q'} B_{Q'}^\dagger (\delta_{Q-Q} - D_{Q-Q}) \\ &= \zeta_Q B_Q^\dagger - \sum_{Q'} \zeta_{Q'} B_{Q'}^\dagger D_{Q-Q} \end{aligned} \quad (7.6)$$

When combined with Eq. (7.5), we readily get Eq. (7.2), with S_Q^\dagger given by

$$S_Q^\dagger = - \sum_{Q'} \zeta_{Q'} B_{Q'}^\dagger D_{Q-Q} = - \sum_{Q'} B_{Q'}^\dagger \zeta_{Q'} (\Delta_{Q-Q'}^{(e)} + \Delta_{Q-Q'}^{(h)}) \quad (7.7)$$

ζ_Q appearing in S_Q^\dagger is defined in Eq. (2.23). It has a constant contribution $(-\varepsilon_0)$ which comes from the neutrality potential V_{intra} induced by intrasite Coulomb interactions. It also has a contribution \mathcal{V}_Q which comes from electron-hole exchange interactions between sites which allow to delocalize the excitation. As shown below, the interaction scatterings generated by these two contributions have rather different properties; this is why it is physically relevant to split S_Q^\dagger as

$$S_Q^\dagger = N_Q^\dagger + T_Q^\dagger \quad (7.8)$$

where N_Q^\dagger and T_Q^\dagger read as S_Q^\dagger in Eq. (7.7), with $\zeta_{Q'}$ replaced by $(-\varepsilon_0)$ and $\mathcal{V}_{Q'}$ respectively.

C. Interacting exciton creation potential

We now turn to the creation potential induced by direct processes through V_{coul} . This interaction contains three parts. The electron-electron contribution gives

$$[V_{ee}, B_Q^\dagger] = \left[\frac{1}{2} \sum_{n_1 \neq n_2} V_{\mathbf{R}_{n_1} - \mathbf{R}_{n_2}} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} a_{n_1}^\dagger a_{n_2}^\dagger a_{n_2} a_{n_1}, \sum_m \frac{e^{i\mathbf{Q} \cdot \mathbf{R}_m}}{\sqrt{N_s}} a_m^\dagger b_m^\dagger \right] \quad (7.9)$$

By using $[a_{n_1}^\dagger a_{n_2}^\dagger a_{n_2} a_{n_1}, a_m^\dagger b_m^\dagger] = a_m^\dagger b_m^\dagger (\delta_{n_1 m} a_{n_2}^\dagger a_{n_2} + \delta_{n_2 m} a_{n_1}^\dagger a_{n_1})$ and by writing $a_m^\dagger b_m^\dagger$ in terms of excitons through Eq. (3.10), we find, since $V_{\mathbf{R}} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} = V_{-\mathbf{R}} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$

$$[V_{ee}, B_Q^\dagger] = \sum_{Q'} B_{Q'}^\dagger \sum_n a_n^\dagger a_n e^{i(\mathbf{Q}-\mathbf{Q}') \cdot \mathbf{R}_n} \sum_{m \neq n} \frac{e^{i(\mathbf{Q}-\mathbf{Q}') \cdot (\mathbf{R}_m - \mathbf{R}_n)}}{N_s} V_{\mathbf{R}_n - \mathbf{R}_m} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \quad (7.10)$$

The last sum does not depend on n due to the translational invariance of the system; so that the above equation can be rewritten as

$$[V_{ee}, B_Q^\dagger] = \sum_{Q'} B_{Q'}^\dagger \mathcal{W}_{\mathbf{Q}-\mathbf{Q}'}^{(ee)} \Delta_{\mathbf{Q}-\mathbf{Q}'}^{(e)} \quad (7.11)$$

where $\mathcal{W}_{\mathbf{Q}}^{(ee)}$ is very similar to the \mathbf{Q} component of the exciton energy \mathcal{V}_Q given in Eq. (2.15), except that it reads in terms of direct Coulomb interactions between two excited atomic levels $\nu = 1$. Its precise value is given by

$$\mathcal{W}_{\mathbf{Q}}^{(ee)} = \sum_{\mathbf{R} \neq 0} e^{-i\mathbf{Q} \cdot \mathbf{R}} V_{\mathbf{R}} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \quad (7.12)$$

In the same way, the hole-hole contribution of V_{coul} leads to

$$[V_{hh}, B_Q^\dagger] = \sum_{Q'} B_{Q'}^\dagger \mathcal{W}_{\mathbf{Q}-\mathbf{Q}'}^{(hh)} \Delta_{\mathbf{Q}-\mathbf{Q}'}^{(h)} \quad (7.13)$$

where $\mathcal{W}_{\mathbf{Q}}^{(hh)}$ reads as $\mathcal{W}_{\mathbf{Q}}^{(ee)}$ with $V_{\mathbf{R}} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$ replaced by $V_{\mathbf{R}} \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$.

If we now turn to electron-hole direct interaction, its commutator with $B_{\mathbf{Q}}^{\dagger}$ gives

$$\left[V_{eh}^{(dir)}, B_{\mathbf{Q}}^{\dagger} \right] = \left[- \sum_{n \neq n'} V_{\mathbf{R}_n - \mathbf{R}_{n'}} \begin{pmatrix} 1 & 1 \\ 0 & 0 \end{pmatrix} b_n^{\dagger} a_{n'}^{\dagger} a_{n'} b_n, \sum_m \frac{e^{i\mathbf{Q} \cdot \mathbf{R}_m}}{\sqrt{N_s}} a_m^{\dagger} b_m^{\dagger} \right] \quad (7.14)$$

To calculate it, we use $\left[b_n^{\dagger} a_{n'}^{\dagger} a_{n'} b_n, a_m^{\dagger} b_m^{\dagger} \right] = a_m^{\dagger} b_m^{\dagger} (\delta_{nm} \delta_{n'm} + \delta_{nm} a_{n'}^{\dagger} a_{n'} + \delta_{n'm} b_n^{\dagger} b_n)$. The first term of this commutator gives 0 for $n \neq n'$. In the two other terms, we rewrite $a_m^{\dagger} b_m^{\dagger}$ in terms of excitons according to Eq. (2.18) and we make appearing $e^{i(\mathbf{Q}-\mathbf{Q}') \cdot (\mathbf{R}_m - \mathbf{R}_n)}$ in the remaining sum to possibly use the translational invariance of the system. This ultimately leads to

$$\left[V_{eh}^{(dir)}, B_{\mathbf{Q}}^{\dagger} \right] = - \sum_{\mathbf{Q}'} B_{\mathbf{Q}'}^{\dagger} \sum_n \left(\mathcal{W}_{\mathbf{Q}-\mathbf{Q}'}^{(eh)} \Delta_{\mathbf{Q}-\mathbf{Q}'}^{(e)} + \mathcal{W}_{\mathbf{Q}-\mathbf{Q}'}^{(he)} \Delta_{\mathbf{Q}-\mathbf{Q}'}^{(h)} \right) \quad (7.15)$$

where $\mathcal{W}_{\mathbf{Q}}^{(eh)}$ and $\mathcal{W}_{\mathbf{Q}}^{(he)}$ read as $\mathcal{W}_{\mathbf{Q}}^{(ee)}$ given in Eq. (7.12) with $V_{\mathbf{R}} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$ replaced by $V_{\mathbf{R}} \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$ and $V_{\mathbf{R}} \begin{pmatrix} 0 & 0 \\ 1 & 1 \end{pmatrix}$ respectively.

By collecting these three contributions, we find that $W_{\mathbf{Q}}^{\dagger} = \left[V_{coul}, B_{\mathbf{Q}}^{\dagger} \right]$ reads as

$$W_{\mathbf{Q}}^{\dagger} = \sum_{\mathbf{Q}'} B_{\mathbf{Q}'}^{\dagger} \left(\mathcal{W}_{\mathbf{Q}-\mathbf{Q}'}^{(e)} \Delta_{\mathbf{Q}-\mathbf{Q}'}^{(e)} + \mathcal{W}_{\mathbf{Q}-\mathbf{Q}'}^{(h)} \Delta_{\mathbf{Q}-\mathbf{Q}'}^{(h)} \right) \quad (7.16)$$

where the prefactors are such that $\mathcal{W}_{\mathbf{Q}}^{(e)} = \mathcal{W}_{\mathbf{Q}}^{(ee)} - \mathcal{W}_{\mathbf{Q}}^{(eh)}$ while $\mathcal{W}_{\mathbf{Q}}^{(h)} = \mathcal{W}_{\mathbf{Q}}^{(hh)} - \mathcal{W}_{\mathbf{Q}}^{(he)}$; so that

$$\mathcal{W}_{\mathbf{Q}}^{(e)} = \sum_{\mathbf{R} \neq \mathbf{0}} e^{-i\mathbf{Q} \cdot \mathbf{R}} \left[V_{\mathbf{R}} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} - V_{\mathbf{R}} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \right] \quad (7.17)$$

$$\mathcal{W}_{\mathbf{Q}}^{(h)} = \sum_{\mathbf{R} \neq \mathbf{0}} e^{-i\mathbf{Q} \cdot \mathbf{R}} \left[V_{\mathbf{R}} \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} - V_{\mathbf{R}} \begin{pmatrix} 0 & 0 \\ 1 & 1 \end{pmatrix} \right] \quad (7.18)$$

D. Discussion

It is of importance to note that, while the structure of the two parts $S_{\mathbf{Q}}^{\dagger}$ and $W_{\mathbf{Q}}^{\dagger}$ of the Frenkel exciton creation potential $V_{\mathbf{Q}}^{\dagger}$ are rather similar, the prefactors of $B_{\mathbf{Q}'}^{\dagger}$ in $W_{\mathbf{Q}}^{\dagger}$ which come from *direct* Coulomb processes between electrons and holes of different sites, depend on the momentum transfer $\mathbf{Q} - \mathbf{Q}'$ only, while this is not true for the prefactor of $B_{\mathbf{Q}'}^{\dagger}$ in $S_{\mathbf{Q}}^{\dagger}$ which comes from "electron-hole exchange", i.e., *indirect* Coulomb processes between atomic levels. This result, which may appear as very strange at first, is linked to the fact that these indirect Coulomb processes do not lead to a momentum transfer: Indeed, the potential S_X they produce is a one-body *diagonal* operator in the exciton subspace, as seen from Eq. (2.22).

Let us recall that the Coulomb exchange processes producing $S_{\mathbf{Q}}^{\dagger}$ in which one electron is excited while the other returns to its ground state, are usually neglected in the case of Wannier excitons. Being much smaller than the direct scatterings due to the orthogonality of the ground and excited state wave functions, they just produce the small energy splitting which exists between dark and bright excitons, when the spin degrees of freedom of these Wannier excitons are included. In the case of Frenkel excitons, the prefactors in $S_{\mathbf{Q}}^{\dagger}$ are also small compared to the ones coming from direct processes since through $V_{\mathbf{R}} \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$, they also contain overlaps of different atomic states $\nu = 0$ and $\nu = 1$ - which are orthogonal - while the prefactors of $W_{\mathbf{Q}}^{\dagger}$ contain $V_{\mathbf{R}} \begin{pmatrix} \nu & \nu' \\ \nu' & \nu \end{pmatrix}$, i.e., overlaps of identical atomic states, ν or ν' . However, these indirect Coulomb processes are crucial for Frenkel excitons since, in the tight binding limit, they are the only processes allowing to delocalize the excitation, as necessary to produce the exciton.

VIII. INTERACTION SCATTERINGS

A. Definition

The interaction scatterings of the two Frenkel excitons ($\mathbf{Q}_1, \mathbf{Q}_2$) are defined through the creation potential $V_{\mathbf{Q}}^\dagger$ as

$$\left[V_{\mathbf{Q}_1}^\dagger, B_{\mathbf{Q}_2}^\dagger \right] = \sum_{\mathbf{Q}'_1 \mathbf{Q}'_2} \xi \left(\begin{smallmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{smallmatrix} \right) B_{\mathbf{Q}'_1}^\dagger B_{\mathbf{Q}'_2}^\dagger \quad (8.1)$$

Before going further, let us recall that this equation, when used for Wannier excitons, does not unambiguously define [20] the interaction scattering $\xi \left(\begin{smallmatrix} n & j \\ m & i \end{smallmatrix} \right)$ between (i, j) and (m, n) states. Indeed, due to the two possible ways to write two excitons leading to Eq. (4.8), it is always possible to replace $\xi \left(\begin{smallmatrix} n & j \\ m & i \end{smallmatrix} \right)$ in Eq. (8.1) by minus the "in" exchange interaction scattering defined as

$$\xi^{in} \left(\begin{smallmatrix} n & j \\ m & i \end{smallmatrix} \right) = \sum_{p \ q} \lambda \left(\begin{smallmatrix} n & q \\ m & p \end{smallmatrix} \right) \xi \left(\begin{smallmatrix} q & j \\ p & i \end{smallmatrix} \right) \quad (8.2)$$

or even by $\left[a\xi \left(\begin{smallmatrix} n & j \\ m & i \end{smallmatrix} \right) - b\xi^{in} \left(\begin{smallmatrix} n & j \\ m & i \end{smallmatrix} \right) \right]$ with $a + b = 1$.

In contrast, due to the fact that there is only one way to construct two Frenkel excitons out of two electron-hole pairs, an equation like Eq. (4.8) does not exist for Frenkel excitons. This leads us to think that the value of the interaction scattering $\xi \left(\begin{smallmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{smallmatrix} \right)$ obtained through Eq. (8.1) must be unique. As a direct consequence, the "in" exchange interaction scattering for Frenkel excitons must be equal to zero. A way to show it, is to insert the closure relation (6.7) for two Frenkel exciton states in front of RHS of Eq. (8.1) acting on vacuum. We find

$$\sum_{\mathbf{Q}'_1 \mathbf{Q}'_2} \xi \left(\begin{smallmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{smallmatrix} \right) B_{\mathbf{Q}'_1}^\dagger B_{\mathbf{Q}'_2}^\dagger |v\rangle = \sum_{\mathbf{P}_1 \mathbf{P}_2} \hat{\xi} \left(\begin{smallmatrix} \mathbf{P}_2 & \mathbf{Q}_2 \\ \mathbf{P}_1 & \mathbf{Q}_1 \end{smallmatrix} \right) B_{\mathbf{P}_1}^\dagger B_{\mathbf{P}_2}^\dagger |v\rangle \quad (8.3)$$

where the scattering appearing in the sum is given by

$$\hat{\xi} \left(\begin{smallmatrix} \mathbf{P}_2 & \mathbf{Q}_2 \\ \mathbf{P}_1 & \mathbf{Q}_1 \end{smallmatrix} \right) = \frac{1}{2} \sum_{\mathbf{Q}'_1 \mathbf{Q}'_2} \xi \left(\begin{smallmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{smallmatrix} \right) \langle v | B_{\mathbf{P}_2} B_{\mathbf{P}_1} B_{\mathbf{Q}'_1}^\dagger B_{\mathbf{Q}'_2}^\dagger | v \rangle \quad (8.4)$$

If we now use Eq. (5.2) for the scalar product of two Frenkel exciton states and we symmetrize the interaction scattering, $\xi \left(\begin{smallmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{smallmatrix} \right) = \xi \left(\begin{smallmatrix} \mathbf{Q}'_1 & \mathbf{Q}_2 \\ \mathbf{Q}'_2 & \mathbf{Q}_1 \end{smallmatrix} \right)$, as always possible since $B_{\mathbf{Q}'_1}^\dagger B_{\mathbf{Q}'_2}^\dagger = B_{\mathbf{Q}'_2}^\dagger B_{\mathbf{Q}'_1}^\dagger$, we find that $\hat{\xi} \left(\begin{smallmatrix} \mathbf{P}_2 & \mathbf{Q}_2 \\ \mathbf{P}_1 & \mathbf{Q}_1 \end{smallmatrix} \right)$ is just

$$\hat{\xi} \left(\begin{smallmatrix} \mathbf{P}_2 & \mathbf{Q}_2 \\ \mathbf{P}_1 & \mathbf{Q}_1 \end{smallmatrix} \right) = \xi \left(\begin{smallmatrix} \mathbf{P}_2 & \mathbf{Q}_2 \\ \mathbf{P}_1 & \mathbf{Q}_1 \end{smallmatrix} \right) - \xi^{in} \left(\begin{smallmatrix} \mathbf{P}_2 & \mathbf{Q}_2 \\ \mathbf{P}_1 & \mathbf{Q}_1 \end{smallmatrix} \right) \quad (8.5)$$

where $\xi^{in} \left(\begin{smallmatrix} \mathbf{P}_2 & \mathbf{Q}_2 \\ \mathbf{P}_1 & \mathbf{Q}_1 \end{smallmatrix} \right)$ is the "in" exchange interaction scattering of two Frenkel excitons, defined in the same way as for Wannier excitons, namely

$$\xi^{in} \left(\begin{smallmatrix} \mathbf{P}_2 & \mathbf{Q}_2 \\ \mathbf{P}_1 & \mathbf{Q}_1 \end{smallmatrix} \right) = \sum_{\mathbf{Q}'_1 \mathbf{Q}'_2} \lambda \left(\begin{smallmatrix} \mathbf{P}_2 & \mathbf{Q}'_2 \\ \mathbf{P}_1 & \mathbf{Q}'_1 \end{smallmatrix} \right) \xi \left(\begin{smallmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{smallmatrix} \right) \quad (8.6)$$

By inserting $\hat{\xi}$ given in Eq. (8.5) into Eq. (8.3), we are led to conclude that $\xi^{in} \left(\begin{smallmatrix} \mathbf{P}_2 & \mathbf{Q}_2 \\ \mathbf{P}_1 & \mathbf{Q}_1 \end{smallmatrix} \right) = 0$, or if ξ^{in} has a non zero part, its contribution to the sum (8.3) must give zero.

Let us now see how this conclusion, based on very general properties of Frenkel excitons, can be recovered through hard algebra.

B. Calculation of the interaction scattering

To calculate the interaction scattering $\xi \left(\begin{smallmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{smallmatrix} \right)$ defined in Eq. (8.1), with the creation potential $V_{\mathbf{Q}}^\dagger$ given in Eq. (7.4), we first note that

$$\left[\Delta_{\mathbf{P}}^{(e)}, B_{\mathbf{Q}}^\dagger \right] = \left[\frac{1}{N_s} \sum_n e^{i\mathbf{P} \cdot \mathbf{R}_n} a_n^\dagger a_n, \frac{1}{\sqrt{N_s}} \sum_m e^{i\mathbf{Q} \cdot \mathbf{R}_m} a_m^\dagger b_m^\dagger \right]$$

$$= \frac{1}{N_s \sqrt{N_s}} \sum_m e^{i(\mathbf{P}+\mathbf{Q}) \cdot \mathbf{R}_m} a_m^\dagger b_m^\dagger \quad (8.7)$$

So that, by writing free electron-hole operators in terms of excitons according to Eq. (2.18), and by using Eq. (2.20), we end with

$$[\Delta_{\mathbf{P}}^{(e)}, B_{\mathbf{Q}}^\dagger] = \frac{1}{N_s} B_{\mathbf{P}+\mathbf{Q}}^\dagger = [\Delta_{\mathbf{P}}^{(h)}, B_{\mathbf{Q}}^\dagger] \quad (8.8)$$

This readily shows that

$$[S_{\mathbf{Q}_1}^\dagger, B_{\mathbf{Q}_2}^\dagger] = -\frac{2}{N_s} \sum_{\mathbf{Q}'_1} \zeta_{\mathbf{Q}'_1} B_{\mathbf{Q}'_1}^\dagger B_{\mathbf{Q}_1+\mathbf{Q}_2-\mathbf{Q}'_1}^\dagger \quad (8.9)$$

$$[W_{\mathbf{Q}_1}^\dagger, B_{\mathbf{Q}_2}^\dagger] = \frac{1}{N_s} \sum_{\mathbf{Q}'_1} \mathcal{W}_{\mathbf{Q}_1-\mathbf{Q}'_1} B_{\mathbf{Q}'_1}^\dagger B_{\mathbf{Q}_1+\mathbf{Q}_2-\mathbf{Q}'_1}^\dagger \quad (8.10)$$

where $\zeta_{\mathbf{Q}}$ is defined in Eq. (2.23) while $\mathcal{W}_{\mathbf{Q}}$ is equal to $\mathcal{W}_{\mathbf{Q}}^{(e)} + \mathcal{W}_{\mathbf{Q}}^{(h)}$; so that

$$\begin{aligned} \mathcal{W}_{\mathbf{Q}} &= \sum_{\mathbf{R} \neq \mathbf{0}} e^{-i\mathbf{Q} \cdot \mathbf{R}} \left[V_{\mathbf{R}} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} + V_{\mathbf{R}}^* \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} - V_{\mathbf{R}} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} - V_{\mathbf{R}}^* \begin{pmatrix} 0 & 0 \\ 1 & 1 \end{pmatrix} \right] \\ &= \mathcal{W}_{\mathbf{Q}}^* = \mathcal{W}_{-\mathbf{Q}} \end{aligned} \quad (8.11)$$

It contains all possible direct interactions between electrons and holes in different sites. This quantity is real, since $V_{\mathbf{R}} \begin{pmatrix} \nu & \nu \\ \nu & \nu \end{pmatrix} = V_{-\mathbf{R}} \begin{pmatrix} \nu & \nu \\ \nu & \nu \end{pmatrix}$ while $V_{\mathbf{R}}^* \begin{pmatrix} 1 & 1 \\ 0 & 0 \end{pmatrix} = V_{-\mathbf{R}} \begin{pmatrix} 0 & 0 \\ 1 & 1 \end{pmatrix}$. For the same reason, it is an even function of \mathbf{Q} .

From Eqs. (7.4) and (7.8), we are lead to split the interaction scattering defined in Eq. (8.1) into three conceptually different terms

$$\xi \left(\begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix} \right) = \xi_{coul} \left(\begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix} \right) - \xi_{trans} \left(\begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix} \right) + \xi_{neut} \left(\begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix} \right) \quad (8.12)$$

The first contribution which reads

$$\xi_{coul} \left(\begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix} \right) = \frac{1}{N_s} \mathcal{W}_{\mathbf{Q}_1-\mathbf{Q}'_1} \delta_{\mathbf{Q}'_1+\mathbf{Q}'_2, \mathbf{Q}_1+\mathbf{Q}_2} \quad (8.13)$$

only depends on the momentum transfer $\mathbf{Q}_1 - \mathbf{Q}'_1$ produced by the scattering. Through $\mathcal{W}_{\mathbf{Q}}$, this contribution comes from all *direct* Coulomb processes between the excited atomic level $\nu = 1$ and the ground state level $\nu = 0$ of the different sites. This part of the interaction scattering which is represented by the diagram of Fig. 5(a), is very similar to the direct Coulomb scattering of two Wannier excitons.

The two other contributions to the interaction scattering are conceptually new. By symmetrizing Eq. (8.9), it is possible to write them as

$$\xi_{transf} \left(\begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix} \right) = \frac{1}{N_s} (\mathcal{V}_{\mathbf{Q}'_1} + \mathcal{V}_{\mathbf{Q}'_2}) \delta_{\mathbf{Q}'_1+\mathbf{Q}'_2, \mathbf{Q}_1+\mathbf{Q}_2} \quad (8.14)$$

$$\xi_{neut} \left(\begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix} \right) = \frac{2\varepsilon_0}{N_s} \delta_{\mathbf{Q}'_1+\mathbf{Q}'_2, \mathbf{Q}_1+\mathbf{Q}_2} \quad (8.15)$$

These scatterings may appear as very strange at first since they do not depend on the momentum transfer but on the momenta of the two "out" excitons \mathbf{Q}'_1 and \mathbf{Q}'_2 for ξ_{transf} , while ξ_{neut} is completely independent of the momenta of the Frenkel excitons involved in the scattering - which is even stranger.

Actually ξ_{neut} does not play a role in the scattering of two Frenkel excitons. Indeed, when inserted in Eq. (8.1), its contribution gives zero

$$\sum \xi_{neut} \left(\begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix} \right) B_{\mathbf{Q}'_1}^\dagger B_{\mathbf{Q}'_2}^\dagger = 0 \quad (8.16)$$

This can be readily shown by noting that

$$\xi_{neut} \begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix} = 2\varepsilon_0\lambda \begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix} \quad (8.17)$$

and by using Eq. (6.12). Consequently ξ in Eq. (8.1) can as well be replaced by

$$\tilde{\xi} \begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix} = \xi_{coul} \begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix} - \xi_{trans} \begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix} \quad (8.18)$$

If we now turn to ξ_{trans} , given in Eq. (8.14), we can note that, due to Eq. (3.11), it also reads

$$\xi_{trans} \begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix} = (\mathcal{V}_{\mathbf{Q}'_1} + \mathcal{V}_{\mathbf{Q}'_2})\lambda \begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix} \quad (8.19)$$

While its contribution in the sum (8.1) definitely differs from zero, this expression of ξ_{trans} leads us to see it as a "transfer assisted exchange" (see Fig. 5b). And indeed, it appears in the interaction scattering ξ or $\tilde{\xi}$ with the minus sign as for any exchange process. To better grasp this term, we can note that, although the potential S_X from which it originates, is a *one-body* operator in the Frenkel exciton subspace, it can lead to a scattering between *two* excitons thanks to carrier exchanges allowed by the exciton composite nature. Such a scattering ξ_{trans} , which does not exist for Wannier excitons when electron-hole exchange, i.e., valence-conduction Coulomb process, is neglected, is quite specific to Frenkel excitons: Indeed, besides direct Coulomb processes which exist for both excitons, Frenkel excitons in addition have indirect Coulomb processes which provide other energy-like quantities from which this novel energy-like scattering can be constructed, by mixing them with carrier exchanges.

It can be of interest to relate this ξ_{trans} scattering to the novel scattering we have identified between two polaritons [18] - we called "photon assisted exchange". For polaritons, the Pauli scattering induced by carrier exchanges between the exciton components, is mixed with the Rabi coupling between photon and exciton, which also is a relevant energy-like quantity appearing in the one-body part of the polariton hamiltonian. As for this photon assisted exchange, the strange asymmetry between "in" and "out" states of assisted exchange scatterings is actually cured in real physical processes in which energy is conserved since the scatterings with interaction before or after the exchange are then equal, as shown in Section IX.

C. Exchange interaction scatterings

The exchange Coulomb scatterings which are succession of carrier exchange before or after carrier interaction, play a key role for Wannier excitons. They are the dominant scatterings for excitons with close-to-zero momenta. We are going to show that in the case of Frenkel excitons these exchange interaction scatterings reduce to zero

$$\tilde{\xi}^{in} \begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix} = \sum_{\mathbf{P}_1 \mathbf{P}_2} \lambda \begin{pmatrix} \mathbf{Q}'_2 & \mathbf{P}_2 \\ \mathbf{Q}'_1 & \mathbf{P}_1 \end{pmatrix} \tilde{\xi} \begin{pmatrix} \mathbf{P}_2 & \mathbf{Q}_2 \\ \mathbf{P}_1 & \mathbf{Q}_1 \end{pmatrix} = 0 \quad (8.20)$$

By using Eq. (3.11) for the Pauli scattering, we readily find that the "in" exchange scattering associated to direct Coulomb processes given in Eq. (8.13) reduces to zero

$$\xi_{coul}^{in} \begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix} = \frac{1}{N_s^2} \delta_{\mathbf{Q}'_1 + \mathbf{Q}'_2, \mathbf{Q}_1 + \mathbf{Q}_2} \sum_{\mathbf{Q}} \mathcal{W}_{\mathbf{Q}} = 0 \quad (8.21)$$

due to Eq. (2.19), namely $\sum_{\mathbf{Q}} e^{i\mathbf{Q} \cdot \mathbf{R}} = N_s \delta_{\mathbf{R}, \mathbf{0}}$ since the $\mathbf{R} = \mathbf{0}$ term are also missing for the sums which enter $\mathcal{W}_{\mathbf{Q}}$ (see Eq. (8.11)).

In the same way, the "in" exchange scattering associated to the transfer part of the interaction given in Eq. (8.14) reduces to zero

$$\xi_{trans}^{in} \begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix} = \frac{1}{N_s^2} \delta_{\mathbf{Q}'_1 + \mathbf{Q}'_2, \mathbf{Q}_1 + \mathbf{Q}_2} \sum_{\mathbf{Q}} (\mathcal{V}_{\mathbf{Q}_1 + \mathbf{Q}} + \mathcal{V}_{\mathbf{Q}_2 - \mathbf{Q}}) = 0 \quad (8.22)$$

since the $\mathbf{R} = \mathbf{0}$ term is also missing from the sum entering $\mathcal{V}_{\mathbf{Q}}$ (see Eq. (2.15)).

We thus conclude that, as obtained from very general arguments at the beginning of this section, the "in" exchange scattering for the first two parts of $\xi \begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix}$, namely $\xi_{coul}^{in} \begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix}$ and $\xi_{trans}^{in} \begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix}$ reduce to zero while the third part ξ_{neut} gives zero when inserted in the relevant sum (see Eq. (8.16)). This physically means that the energy-like part of the Frenkel exciton scattering is only controlled by direct Coulomb processes *and* by transfer assisted exchange, a result not obvious at first.

IX. FRENKEL EXCITON HAMILTONIAN IN THE TWO-EXCITON SUBSPACE

A. H_X acting on two excitons

In order to better grasp the interplay between the various scatterings appearing in the preceding sections, let us calculate the matrix element of the interacting exciton Hamiltonian in the two-exciton subspace. Using Eq. (7.1), we find that H_X acting on two Frenkel excitons gives

$$H_X B_{\mathbf{Q}_1}^\dagger B_{\mathbf{Q}_2}^\dagger |v\rangle = \left(B_{\mathbf{Q}_1}^\dagger H_X + E_{\mathbf{Q}_1} B_{\mathbf{Q}_1}^\dagger + V_{\mathbf{Q}_1}^\dagger \right) B_{\mathbf{Q}_2}^\dagger |v\rangle \quad (9.1)$$

Due to Eq. (8.1), this also reads

$$\begin{aligned} & (H_X - E_{\mathbf{Q}_1} - E_{\mathbf{Q}_2}) B_{\mathbf{Q}_1}^\dagger B_{\mathbf{Q}_2}^\dagger |v\rangle \\ &= V_{\mathbf{Q}_1}^\dagger B_{\mathbf{Q}_2}^\dagger |v\rangle = \sum_{\mathbf{P}_1 \mathbf{P}_2} \xi \left(\begin{smallmatrix} \mathbf{P}_2 & \mathbf{Q}_2 \\ \mathbf{P}_1 & \mathbf{Q}_1 \end{smallmatrix} \right) B_{\mathbf{P}_1}^\dagger B_{\mathbf{P}_2}^\dagger |v\rangle \end{aligned} \quad (9.2)$$

where ξ can be possibly replaced by $\tilde{\xi}$ defined in Eq. (8.18), due to Eq. (8.16).

B. Matrix element of H_X in the two-exciton subspace

We now turn to the matrix element of the interacting exciton Hamiltonian H_X in the two exciton subspace. With H_X acting on the right, we find

$$\begin{aligned} \langle v | B_{\mathbf{Q}_2'} B_{\mathbf{Q}_1'} H_X B_{\mathbf{Q}_1}^\dagger B_{\mathbf{Q}_2}^\dagger |v\rangle &= (E_{\mathbf{Q}_1} + E_{\mathbf{Q}_2}) \langle v | B_{\mathbf{Q}_2'} B_{\mathbf{Q}_1'} B_{\mathbf{Q}_1}^\dagger B_{\mathbf{Q}_2}^\dagger |v\rangle \\ &+ \sum_{\mathbf{P}_1 \mathbf{P}_2} \langle v | B_{\mathbf{Q}_2'} B_{\mathbf{Q}_1'} B_{\mathbf{P}_1}^\dagger B_{\mathbf{P}_2}^\dagger |v\rangle \tilde{\xi} \left(\begin{smallmatrix} \mathbf{P}_2 & \mathbf{Q}_2 \\ \mathbf{P}_1 & \mathbf{Q}_1 \end{smallmatrix} \right) \end{aligned} \quad (9.3)$$

If we now use the scalar product of two-exciton states given in Eq. (5.2), the first term of Eq. (9.3) reduces to

$$(E_{\mathbf{Q}_1} + E_{\mathbf{Q}_2}) \left(\delta_{\mathbf{Q}_1' \mathbf{Q}_1} \delta_{\mathbf{Q}_2' \mathbf{Q}_2} + \delta_{\mathbf{Q}_1' \mathbf{Q}_2} \delta_{\mathbf{Q}_2' \mathbf{Q}_1} - \frac{2}{N_s} \delta_{\mathbf{Q}_1' + \mathbf{Q}_2', \mathbf{Q}_1 + \mathbf{Q}_2} \right) \quad (9.4)$$

To calculate the second term, we use the same scalar product and take into account that the exchange scatterings reduce to zero according to Eq. (8.20). This second term then reads

$$\tilde{\xi} \left(\begin{smallmatrix} \mathbf{Q}_2' & \mathbf{Q}_2 \\ \mathbf{Q}_1' & \mathbf{Q}_1 \end{smallmatrix} \right) + \tilde{\xi} \left(\begin{smallmatrix} \mathbf{Q}_1' & \mathbf{Q}_2 \\ \mathbf{Q}_2' & \mathbf{Q}_1 \end{smallmatrix} \right) = \frac{1}{N_s} (\mathcal{W}_{\mathbf{Q}_1' - \mathbf{Q}_1} + \mathcal{W}_{\mathbf{Q}_2' - \mathbf{Q}_1} - 2\mathcal{V}_{\mathbf{Q}_2'} - 2\mathcal{V}_{\mathbf{Q}_1'}) \delta_{\mathbf{Q}_1' + \mathbf{Q}_2', \mathbf{Q}_1 + \mathbf{Q}_2} \quad (9.5)$$

C. On the asymmetry of transfer assisted exchange scatterings

In order to better accept the asymmetry between "in" and "out" excitons appearing in the transfer assisted exchange scattering, let us now show that these "in" and "out" scatterings are equal when energy is conserved. For that, we use the above equations to calculate the same matrix element $\langle v | B_{\mathbf{Q}_2'} B_{\mathbf{Q}_1'} H_X B_{\mathbf{Q}_1}^\dagger B_{\mathbf{Q}_2}^\dagger |v\rangle$ but through

$$\begin{aligned} & \langle v | B_{\mathbf{Q}_2} B_{\mathbf{Q}_1} H_X B_{\mathbf{Q}_1'}^\dagger B_{\mathbf{Q}_2'}^\dagger |v\rangle^* \\ &= \left(E_{\mathbf{Q}_1'}^* + E_{\mathbf{Q}_2'}^* \right) \left(\delta_{\mathbf{Q}_1' \mathbf{Q}_1} \delta_{\mathbf{Q}_2' \mathbf{Q}_2} + \delta_{\mathbf{Q}_1' \mathbf{Q}_2} \delta_{\mathbf{Q}_2' \mathbf{Q}_1} - \frac{2}{N_s} \delta_{\mathbf{Q}_1' + \mathbf{Q}_2', \mathbf{Q}_1 + \mathbf{Q}_2} \right) \\ &+ \frac{1}{N_s} \left(\mathcal{W}_{\mathbf{Q}_1 - \mathbf{Q}_1'}^* + \mathcal{W}_{\mathbf{Q}_2 - \mathbf{Q}_2'}^* - 2\mathcal{V}_{\mathbf{Q}_2}^* - 2\mathcal{V}_{\mathbf{Q}_1}^* \right) \delta_{\mathbf{Q}_1 + \mathbf{Q}_2, \mathbf{Q}_1' + \mathbf{Q}_2'} \end{aligned}$$

By noting that $E_{\mathbf{Q}}$ is real as well as $\mathcal{V}_{\mathbf{Q}}$ (see Eq. (2.15)), while $\mathcal{W}_{\mathbf{Q}}^* = \mathcal{W}_{\mathbf{Q}} = \mathcal{W}_{-\mathbf{Q}}$ (see Eq. (8.11)), and by comparing the two expressions of $\langle v | B_{\mathbf{Q}_2} B_{\mathbf{Q}_1} H_X B_{\mathbf{Q}_1}^\dagger B_{\mathbf{Q}_2}^\dagger | v \rangle$, we readily see that

$$\begin{aligned} & (\mathcal{V}_{\mathbf{Q}_1'} + \mathcal{V}_{\mathbf{Q}_2'} - \mathcal{V}_{\mathbf{Q}_1} - \mathcal{V}_{\mathbf{Q}_2}) \delta_{\mathbf{Q}_1' + \mathbf{Q}_2', \mathbf{Q}_1 + \mathbf{Q}_2} \\ &= (E_{\mathbf{Q}_1'} + E_{\mathbf{Q}_2'} - E_{\mathbf{Q}_1} - E_{\mathbf{Q}_2}) \delta_{\mathbf{Q}_1' + \mathbf{Q}_2', \mathbf{Q}_1 + \mathbf{Q}_2} \end{aligned} \quad (9.7)$$

which also reads

$$\begin{aligned} & \xi_{transf} \begin{pmatrix} \mathbf{Q}_2' & \mathbf{Q}_2 \\ \mathbf{Q}_1' & \mathbf{Q}_1 \end{pmatrix} - \xi_{transf} \begin{pmatrix} \mathbf{Q}_2 & \mathbf{Q}_2' \\ \mathbf{Q}_1 & \mathbf{Q}_1' \end{pmatrix} \\ &= (E_{\mathbf{Q}_1'} + E_{\mathbf{Q}_2'} - E_{\mathbf{Q}_1} - E_{\mathbf{Q}_2}) \lambda \begin{pmatrix} \mathbf{Q}_2' & \mathbf{Q}_2 \\ \mathbf{Q}_1' & \mathbf{Q}_1 \end{pmatrix} \end{aligned} \quad (9.8)$$

This proves that the asymmetry between "in" and "out" states in the transfer term is removed for energy conserving processes which are the ones controlling the physically relevant processes between two Frenkel excitons. A similar result is found for the photon assisted exchange scattering of two polaritons.

D. Hamiltonian expectation value

From Eqs. (5.2) and (9.3-5), we get the Hamiltonian expectation value for two Frenkel excitons as

$$\begin{aligned} & \frac{\langle v | B_{\mathbf{Q}_1} B_{\mathbf{Q}_2} H_X B_{\mathbf{Q}_1}^\dagger B_{\mathbf{Q}_2}^\dagger | v \rangle}{\langle v | B_{\mathbf{Q}_1} B_{\mathbf{Q}_2} B_{\mathbf{Q}_1}^\dagger B_{\mathbf{Q}_2}^\dagger | v \rangle} = E_{\mathbf{Q}_1} + E_{\mathbf{Q}_2} \\ & + \frac{1}{N_s} \frac{\mathcal{W}_0 + \mathcal{W}_{\mathbf{Q}_2 - \mathbf{Q}_1} - 2\mathcal{V}_{\mathbf{Q}_1} - 2\mathcal{V}_{\mathbf{Q}_2}}{1 + \delta_{\mathbf{Q}_1, \mathbf{Q}_2} - \frac{2}{N_s}} \end{aligned} \quad (9.9)$$

So that the Hamiltonian expectation value for two identical excitons $\mathbf{Q}_1 = \mathbf{Q}_2 = \mathbf{Q}$ reduces to

$$\langle H_X \rangle_2 = 2E_{\mathbf{Q}} + \frac{\mathcal{W}_0 - 2\mathcal{V}_{\mathbf{Q}}}{N_s - 1} \quad (9.10)$$

Its interaction part contains a \mathcal{W}_0 contribution which comes from direct Coulomb processes between sites. It also contains an indirect "transfer" contribution induced by the possible fermion exchanges between composite boson excitons. This term which comes from exchange between *two* excitons mixed with excitation transfer has a nature quite different from the one of the direct Coulomb term \mathcal{W}_0 . As $E_{\mathbf{Q}}$, it depends on the momentum \mathbf{Q} of the exciton considered. We see that the interaction part of the Hamiltonian expectation value of two excitons reduces to zero in the large sample limit, i.e., for $N_s \rightarrow \infty$. This is physically reasonable since the interaction of just two excitons in a huge volume cannot change their energy very much. However, as in the case of Wannier excitons, this interaction part is going to appear with a $N(N-1)/2$ prefactor when considering N excitons instead of two, due to the number of ways to choose 2 excitons among N . The precise calculation of the Hamiltonian expectation value for N Frenkel excitons is out of the scope of the present paper.

E. Comparison with elementary bosons

Since many people are still tempted to replace excitons by elementary bosons with a set of "appropriate" effective scatterings dressed by exchanges, let us again show that, as for Wannier excitons, it is not possible to construct such an effective bosonic Hamiltonian for Frenkel excitons, due to possible carrier exchanges between these excitons.

If an effective Hamiltonian were to exist, it would read

$$\bar{H}_X = \sum E_{\mathbf{P}} \bar{B}_{\mathbf{P}}^\dagger \bar{B}_{\mathbf{P}} + \frac{1}{2} \sum \bar{V} \begin{pmatrix} \mathbf{P}_2' & \mathbf{P}_2 \\ \mathbf{P}_1' & \mathbf{P}_1 \end{pmatrix} \bar{B}_{\mathbf{P}_1'}^\dagger \bar{B}_{\mathbf{P}_2'}^\dagger \bar{B}_{\mathbf{P}_2} \bar{B}_{\mathbf{P}_1} \quad (9.11)$$

with $[\bar{B}_{\mathbf{P}'}, \bar{B}_{\mathbf{P}}^\dagger] = \delta_{\mathbf{P}'\mathbf{P}}$ for boson excitons; so that \bar{H}_X acting on two-exciton states would give

$$\begin{aligned} \bar{H}_X \bar{B}_{\mathbf{Q}_1}^\dagger \bar{B}_{\mathbf{Q}_2}^\dagger |v\rangle &= (E_{\mathbf{Q}_1} + E_{\mathbf{Q}_2}) \bar{B}_{\mathbf{Q}_1}^\dagger \bar{B}_{\mathbf{Q}_2}^\dagger |v\rangle \\ &+ \frac{1}{2} \sum \left(\bar{V} \left(\begin{smallmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{smallmatrix} \right) + \bar{V} \left(\begin{smallmatrix} \mathbf{Q}'_2 & \mathbf{Q}_1 \\ \mathbf{Q}'_1 & \mathbf{Q}_2 \end{smallmatrix} \right) \right) \bar{B}_{\mathbf{Q}'_1}^\dagger \bar{B}_{\mathbf{Q}'_2}^\dagger |v\rangle \end{aligned} \quad (9.12)$$

To get the effective scatterings $\bar{V} \left(\begin{smallmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{smallmatrix} \right)$, we can think of comparing this result with H_X acting on two Frenkel excitons. By symmetrizing Eq. (9.2) for $B_{\mathbf{Q}'_1}^\dagger B_{\mathbf{Q}'_2}^\dagger = B_{\mathbf{Q}'_2}^\dagger B_{\mathbf{Q}'_1}^\dagger$, this leads us to take $\bar{V} \left(\begin{smallmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{smallmatrix} \right)$ as $\xi \left(\begin{smallmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{smallmatrix} \right)$ or better as $\tilde{\xi} \left(\begin{smallmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{smallmatrix} \right)$ in order to avoid the spurious constant term $(-2\varepsilon_0)$ in the effective scattering. However, this result is fully unacceptable since the $(\mathcal{V}_{\mathbf{Q}'_1} + \mathcal{V}_{\mathbf{Q}'_2})$ part of ξ_{transf} induces a non-hermiticity in the effective Hamiltonian. Indeed, for \bar{H}_X to be hermitian, we must have

$$\bar{V} \left(\begin{smallmatrix} \mathbf{P}'_2 & \mathbf{P}_2 \\ \mathbf{P}'_1 & \mathbf{P}_1 \end{smallmatrix} \right) = \left[\bar{V} \left(\begin{smallmatrix} \mathbf{P}_2 & \mathbf{P}'_2 \\ \mathbf{P}_1 & \mathbf{P}'_1 \end{smallmatrix} \right) \right]^* \quad (9.13)$$

while ξ_{transf} does not have this property. Consequently, as for Wannier excitons [20], it is not possible to construct an effective bosonic Hamiltonian for Frenkel excitons with the structure given by Eq. (9.11), due to the presence of exchange processes in the matrix element. However, we would like to notice that in Refs. [21, 22, 23] the fermionic Hamiltonian was represented exactly as an *infinite* series expansion in creation and destruction operators for excitations on atomic sites and these operators obey bosonic commutation rules. Note that, within such a scheme, it is rather complicated technically to treat processes involving large number of excitons, as explained in a more detail in Section XI.

X. DISCUSSION

Since Frenkel excitons are made of highly localized electron-hole pairs, we can be led to think that carrier exchanges between Frenkel excitons should be strongly reduced; so that their exciton composite nature should have very little consequences on their many-body physics. To check this basic idea, we are going to make a precise comparison between Frenkel excitons and elementary bosons.

The fact that these excitons are made with electrons and holes localized on the same site, should also make them rather different from Wannier excitons constructed on *delocalized* conduction electrons and valence holes. A precise comparison of the basic properties of Frenkel and Wannier excitons is thus of interest to better grasp the relevant parameters which control the many-body physics of these composite bosons.

A. Comparison with elementary bosons

Let us first compare Frenkel excitons with elementary bosons.

Frenkel excitons are made of indistinguishable electrons and holes. They thus are composite particles. However, due to the fact that the wave functions of these carriers are the ones of highly localized atomic states on the same ion site, there is one way only to construct two excitons out of two electron-hole pairs. This leads to make Frenkel excitons appear as elementary particles. To support this idea, we can mention their closure relation which has the same $(1/N!)$ prefactor as the one for elementary quantum particles.

In spite of these arguments, Frenkel excitons differ from elementary bosons by various means. A very important aspect of their composite nature is the existence of Pauli scatterings $\lambda \left(\begin{smallmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{smallmatrix} \right)$ between two Frenkel excitons induced by carrier exchanges. These dimensionless scatterings in particular appear in the scalar product of two Frenkel exciton states, which does not reduce to a set of Kronecker symbols, as for elementary bosons. The possible carrier exchanges between excitons also produce a normalization factor for N identical excitons which is not $N!$ as for elementary bosons but $N!F_N$ where F_N is not a small correction but decreases exponentially with N . Finally, when mixed with the indirect Coulomb processes responsible for the Frenkel exciton excitation transfer between sites, these dimensionless Pauli scatterings give rise to an energy-like "transfer assisted exchange scatterings" which cannot be properly included in a bosonic effective Hamiltonian for Frenkel excitons without dropping its required hermiticity.

These Frenkel excitons thus are somewhat awkward because they partly behave as elementary particles and partly as composite particles. This makes their handling through intuitive arguments rather dangerous. This is why the

hard algebra based on four commutators proposed in the present many-body theory, appears as highly valuable to overcome any possible uncertainty.

B. Comparison with Wannier excitons

Let us now compare Wannier and Frenkel excitons.

Wannier excitons are constructed on two fully delocalized particles, the conduction electron and the valence hole. The problem is then to make out of these delocalized fermions a bound exciton. This is done through *intraband* Coulomb processes. In contrast, Frenkel excitons are constructed on two fully localized particles, the first atomic excited state of a given site and the absence of atomic ground state electron on the same site. The problem then is to delocalize this highly bound excitation to produce a delocalized excitation. This is done through *interband* Coulomb processes.

Wannier excitons are characterized by a center-of-mass momentum and a relative motion index, the electrons and holes on which these excitons are constructed being two fully delocalized particles. In contrast, Frenkel excitons are only characterized by a center-of-mass momentum since their electrons and holes are not free but forced to be on the same site. Due to this unique degree of freedom, N Frenkel excitons have the $1/N!$ prefactor in their closure relation characteristic for N elementary particles, while the closure relation for Wannier excitons has a prefactor $(1/N!)^2$ which is the signature of the two degrees of freedom of these excitons.

Being both composite particles, they can interact by fermion exchanges through 2×2 Pauli scatterings. These fermion exchanges make the scalar product of N identical excitons differ from their elementary boson value $N!$ by a factor F_N , which, for both excitons, decreases exponentially with $N\eta$. The small dimensionless parameter η associated to density N/L^D which controls these fermion exchanges, appears as $N(a_x/L)^D$ for Wannier excitons, while it appears as N/N_s for Frenkel excitons. This proves that the key parameter for the many-body physics of excitons is not linked to the extension of the electron-hole relative motion wave function as first thought - otherwise η would reduce to zero in the case of Frenkel excitons. In contrast, it must be physically understood as the number excitons at hand divided by the total number of excitons the sample can accommodate, this number being the number of ion sites N_s in the case of Frenkel excitons while it is the ratio $(L/a_x)^D$ of the sample volume to the exciton volume in the case of Wannier excitons.

The Pauli scatterings for Wannier and Frenkel excitons are represented by the same Shiva diagram for carrier exchange between two excitons. This diagram, as well as the ones for carrier exchange between more than two excitons, can be decomposed in terms of 2×2 Pauli scatterings and calculated along the same intuitive line as the one we have established for Wannier excitons. The only "little" problem arises with two consecutive exchanges: Instead of getting an identity, as visually seen, two consecutive exchanges between two Frenkel excitons is found to reduce to an exchange. As a direct consequence, it is not possible to rewrite two Frenkel excitons as a sum of two other Frenkel excitons, as in the case of Wannier excitons. This awkward result on two consecutive exchanges puts some shade on the very visual handling of Shiva diagrams in the case of Frenkel excitons. This is why it seems wise to support all visual results on Shiva diagrams by a hard algebra of the Frenkel exciton matrix element they represent, using the four key commutators of the present many-body theory.

The possible difficulties with Frenkel exciton Shiva diagrams, when compared with Wannier excitons, can be traced back to the fact that the states on which Frenkel excitons are constructed, do not form a clean complete basis for *all* electron-hole pair states due to the tight binding approximation on which these excitons are based. This is why, when summations over intermediate states have to be performed, they not always give the correct results. To predict when these results are incorrect is however not so easy. Thanks to the full proof procedure we have constructed, it is however possible to reach the correct answer through a rather simple algebra based on commutator manipulations.

Besides fermion exchanges, Frenkel and Wannier excitons also feel each other through Coulomb interaction. In addition to direct processes between carriers, indirect processes are also kept for Frenkel excitons since, in the tight-binding limit for electron and hole states, these are the only processes allowing to delocalize the excitation, i.e., to produce the exciton. Although appearing as a one-body operator in the exciton subspace, these indirect "transfer" processes give rise to a novel 2×2 energy-like scattering, when mixed with carrier exchange. These "transfer assisted exchange" scatterings which do not exist for Wannier excitons, are specific to the Frenkel exciton many-body physics. They in particular appear in the matrix element of the Hamiltonian in the two exciton subspace as well as in the Hamiltonian expectation value.

XI. STATE OF THE ART

Some many-body properties of Frenkel excitons have already been studied in the past, see Refs. [21, 22, 23, 24, 25, 26].

(i) Agranovich and coworkers [21, 22, 23], as well as Davydov in Ref. [24], start with a system Hamiltonian written in terms of creation operators a_{0n}^\dagger and a_{1n}^\dagger for ground and first excited states of isolated molecules on site n which is quite similar to our Hamiltonian with a_{0n} essentially replaced by b_n^\dagger . Their fermionic Hamiltonian is then rewritten in terms of excitation operators B_n^\dagger , i.e., products like $a_{1n}^\dagger a_{0n}$. To do so, it is invoked [21] that the sum of the occupation numbers for the ground and first excited states of each molecule is equal to 1. This condition between scalars is then replaced by the same condition between operators, as seen in Eq. (4.9) of Ref. [21], namely

$$\hat{N}_{0n} = 1 - \hat{N}_{1n} \quad (11.1)$$

where $\hat{N}_{fn} = a_{fn}^\dagger a_{fn}$ is the occupation number operator of the state $f = (0, 1)$ in the site n . Eq. (11.1) is valid only when applied to states in which the sum of the occupation numbers for the ground and first excited states of each molecule is equal to 1. This equation (11.1), when implemented to the theory significantly facilitates a final compact form for the Hamiltonian. As seen from Refs. [21, 22], this procedure has however been used for two-exciton problems only. The generalization [23] of this approach to an arbitrary number of excitons turns out to be rather complicated technically, in contrast to our method which is quite straightforward for any number of Frenkel excitons, thanks to Eqs. (3.12, 13).

(ii) Mukamel and coworkers [25, 26, 27, 28] have followed a completely different approach based on the idea that, for problems dealing with a fixed number N of electron-hole pairs, it is always possible to write the system Hamiltonian H as well as the commutators between electron-hole operators $[B_m, B_n^\dagger]$ *exactly*, in terms of *infinite series* of electron-hole operators $B_{n_1}^\dagger \dots B_{n_p}^\dagger B_{m_1} \dots B_{m_p}$, namely

$$H = \sum_{p=1}^{\infty} H^{(p)}$$

$$H^{(p)} = \sum_{\{n\}\{m\}} h^{(p)}(n_1 \dots n_p; m_1 \dots m_p) B_{n_1}^\dagger \dots B_{n_p}^\dagger B_{m_1} \dots B_{m_p} \quad (11.2)$$

and similarly for $[B_m, B_n^\dagger]$. In order to describe a system of N interacting composite excitons, we then have to keep terms in these series for the Hamiltonian and the pair commutator, which contain products up to the $p = N$ and $p = N - 1$, respectively. The constant prefactors in front of all these operators are obtained through the projection of the initial fermionic Hamiltonian and the commutator $[B_m, B_n^\dagger]$ on the N -pair subspace. This method which is formally exact, turns out to be technically quite heavy since the series become more and more complicated with the increase of p . Actually, the authors of Refs. [25, 26, 27, 28] have derived these series for two-exciton problems only, and they have used them to calculate successfully the third order susceptibility $\chi^{(3)}$.

Very recently, we have reconsidered the idea of using infinite series of operators to describe interacting composite excitons [29]. Instead of using free pair operators, like Mukamel and coworkers, we have used correlated pair operators, i.e., excitons which are the relevant operators for such problems. By making use of the exciton closure relation, we have previously derived, we have been able to write the two infinite series explicitly, through rather light calculations. These series read in terms of Pauli and interaction scatterings. However, the proper handling of these two infinite series for N -body problems turn out to be far more cumbersome than the many-body theories for Wannier or Frenkel excitons we have constructed, based on just four commutators.

XII. CONCLUSION

In this paper, we propose a new many-body theory for Frenkel excitons in which the composite nature of these particles is treated exactly, excitons being never bosonized. Starting from the expression of the Frenkel exciton creation operator $B_{\mathbf{Q}}^\dagger$ written in terms of electron and hole creation operators, we derive the commutation rules for these Frenkel excitons. They clearly differ from the ones of elementary bosons due to carrier exchanges induced by the exciton composite nature. These carrier exchanges give rise to "Pauli scatterings" between excitons, similar to the one we found for Wannier excitons. They are represented by the same Shiva diagrams calculated along the same line.

Due to the fact that Frenkel excitons are only characterized by a center-of-mass momentum \mathbf{Q} , their Pauli scatterings take an extremely simple form

$$\lambda \begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix} = \frac{1}{N_s} \delta_{\mathbf{Q}'_1 + \mathbf{Q}'_2, \mathbf{Q}_1 + \mathbf{Q}_2} \quad (12.1)$$

where N_s is the number of ion sites, the many-body physics of N Frenkel excitons being controlled by the small dimensionless parameter

$$\eta = N/N_s \quad (12.2)$$

This parameter is the analog of parameter $\eta = N (a_x/L)^D$ for Wannier excitons since N_s like $(L/a_x)^D$ is the maximum number of excitons the sample can accommodate.

As Frenkel excitons are constructed on highly localized electron-hole pairs, we could expect them to behave as elementary bosons. While their closure relation is indeed the one of elementary bosons - with a prefactor $1/N!$ while the one for Wannier excitons has a prefactor $(1/N!)^2$ - we find that they definitely behave as composite bosons through many other properties. In particular, the normalization factor of N Frenkel excitons $\langle v | B_{\mathbf{Q}}^N B_{\mathbf{Q}}^{\dagger N} | v \rangle = N! F_N$ differs from its elementary boson value $N!$ by a factor

$$F_N = \frac{N_s!}{(N_s - N)! N_s^N} \quad (12.3)$$

which, as for Wannier excitons, decreases exponentially with $N\eta$.

In addition to carrier exchanges, Frenkel excitons also interact through Coulomb processes. The interaction scattering they produce, are derived, as for Wannier excitons, through a set of creation potentials. The part of the interaction scattering coming from direct Coulomb processes between sites depends on the momentum transfer as

$$\xi_{coul} \begin{pmatrix} \mathbf{Q}_2 - \mathbf{Q}' & \mathbf{Q}_2 \\ \mathbf{Q}_1 + \mathbf{Q} & \mathbf{Q}_1 \end{pmatrix} = \frac{1}{N_s} \delta_{\mathbf{Q} \mathbf{Q}'} \mathcal{W}_{\mathbf{Q}} \quad (12.4)$$

$$\mathcal{W}_{\mathbf{Q}} = \sum_{\mathbf{R} \neq \mathbf{0}} e^{-i\mathbf{Q} \cdot \mathbf{R}} \left[V_{\mathbf{R}} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} + V_{\mathbf{R}} \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} - V_{\mathbf{R}} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - V_{\mathbf{R}} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \right] \quad (12.5)$$

where $V_{\mathbf{R}} \begin{pmatrix} \nu'_2 & \nu_2 \\ \nu'_1 & \nu_1 \end{pmatrix}$ is the matrix element of the Coulomb potential between atomic sites at \mathbf{R} , one electron going from the atomic state ν_1 to ν'_1 while the other goes from ν_2 to ν'_2 (see Eq. (2.6)).

Besides this rather standard interaction scattering, we have identified a novel "transfer assisted exchange" scattering which has similarity with "photon assisted exchange" we found between polaritons. It comes from the indirect Coulomb processes responsible for the excitation transfer of Frenkel excitons, the coupling between two excitons being made through the Pauli scattering for carrier exchanges between these excitons. This "transfer assisted exchange" scattering depends on the "out" momenta ($\mathbf{Q}'_1, \mathbf{Q}'_2$) but not on the momentum transfer ($\mathbf{Q}'_1 - \mathbf{Q}_1$) since the excitation transfer does not induce any momentum change. Its precise value reads

$$\xi_{transf} \begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix} = (\mathcal{V}_{\mathbf{Q}'_1} + \mathcal{V}_{\mathbf{Q}'_2}) \lambda \begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix} \quad (12.6)$$

where $\mathcal{V}_{\mathbf{Q}}$ is the \mathbf{Q} dependent part of the exciton energy.

$$\mathcal{V}_{\mathbf{Q}} = \sum_{\mathbf{R} \neq \mathbf{0}} e^{-i\mathbf{Q} \cdot \mathbf{R}} V_{\mathbf{R}} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (12.7)$$

It is possible to show that, in this transfer assisted exchange, symmetry between "in" and "out" states is restored for energy conserving processes since we do have

$$\begin{aligned} & \xi_{transf} \begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix} - \xi_{transf} \begin{pmatrix} \mathbf{Q}_2 & \mathbf{Q}'_2 \\ \mathbf{Q}_1 & \mathbf{Q}'_1 \end{pmatrix} \\ &= (E_{\mathbf{Q}'_1} + E_{\mathbf{Q}'_2} - E_{\mathbf{Q}_1} - E_{\mathbf{Q}_2}) \lambda \begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix} \end{aligned} \quad (12.8)$$

Due to this "transfer assisted exchange" scattering, here also it is not possible to construct an effective bosonic Hamiltonian for Frenkel excitons which is hermitian, as physically required, and which produces the same matrix element as the one of the exact fermionic Hamiltonian.

Frenkel excitons turn out to be quite tricky bosons: they appear as elementary in some cases but composite in many others. This is why it seems hard to guess physical results like the scattering rate of Frenkel excitons, the ground state energy of N Frenkel excitons or the nonlinear susceptibilities of materials having such excitons, without a precise calculation of these quantities using the procedure developed in this paper. These problems will be addressed in a near future.

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Figure captions

- Fig 1. (a) Electron-hole pair eigenstate $a_{n_e}^\dagger b_{n_h}^\dagger |v\rangle$ of H_{eh} defined in Eq. (2.3).
 (b) Electron-hole pair eigenstate $a_n^\dagger b_n^\dagger |v\rangle$ of H_{pair} defined in Eq. (2.4).
 (c) Indirect Coulomb potential V_{trans} as defined in Eq. (2.10) which allows to transfer the excitation from site n_2 to site n_1 .
 (d, e, h) Direct Coulomb potentials V_{eh} , V_{ee} and V_{hh} as defined in Eqs. (2.26-28).
 Fig 2. (a) Shiva diagram for the Pauli scattering $\lambda \left(\begin{smallmatrix} \mathbf{Q}' & \mathbf{Q} \\ \mathbf{P}' & \mathbf{P} \end{smallmatrix} \right)$ of two "in" Frenkel excitons (\mathbf{P} , \mathbf{Q}) toward two "out" excitons (\mathbf{P}' , \mathbf{Q}') as defined in Eqs. (3.11) and (4.2, 4.4).
 (b) Shiva diagram for carrier exchange of three Frenkel excitons defined in Eq. (4.5) and its decomposition in 2×2 Pauli scatterings as given in Eq. (4.6).
 (c) Same as (b) for four excitons.

(d) Two consecutive carrier exchanges should reduce to an identity as seen from Fig. 2(e), while two consecutive Pauli scatterings do not reduce to this identity, as seen from Eq. (4.7).

Fig 3. Shiva diagram for the scalar product of two Frenkel exciton states, as given in Eq. (5.2).

Fig 4. Shiva diagram for the scalar product of three Frenkel exciton states as given in Eq. (5.5).

Fig 5. (a) Part of the interaction scattering $\xi_{coul} \begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix}$ associated to direct Coulomb processes between electrons and holes of different sites defined in Eq. (8.13).

(b) Part of the interaction scattering $\xi_{trans} \begin{pmatrix} \mathbf{Q}'_2 & \mathbf{Q}_2 \\ \mathbf{Q}'_1 & \mathbf{Q}_1 \end{pmatrix}$ associated to the indirect Coulomb processes insuring the excitation transfer defined in Eq. (8.14). This conceptually new scattering can be seen as a "transfer assisted exchange", similar to the "photon assisted exchange" scattering we have identified between two polaritons.